PB-251 418

# AMMONIA REMOVAL FROM WASTEWATER BY LIGAND EXCHANGE

Lloyd M. Smith, et al

Gillette Company Research Institute

Prepared for:

Municipal Environmental Research Laboratory

April 1976

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**TECHNICAL REPORT DATA**
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| 1. REPORT NO. | 2. | 3. PB 251 418 |
|---|---|---|
| EPA-600/2-76-103 | | |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| AMMONIA REMOVAL FROM WASTEWATER BY LIGAND EXCHANGE | April 1976 (Issuing Date) |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) | 8. PERFORMING ORGANIZATION REPORT NO. |
| Lloyd M. Smith, George A. Lyerly, Marilyn E. Dooley | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEMENT NO. |
| GILLETTE RESEARCH INSTITUTE<br>1413 Research Boulevard<br>Rockville, Maryland 20850 | 1BC611 |
| | 11. CONTRACT/GRANT NO. |
| | 68-03-0455 |
| 12. SPONSORING AGENCY NAME AND ADDRESS | 13. TYPE OF REPORT AND PERIOD COVERED |
| Municipal Environmental Research Laboratory<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Cincinnati, Ohio 45268 | 14. SPONSORING AGENCY CODE<br>EPA-ORD |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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Initially, the capacity of the hydrous zirconium oxide for copper was examined to determine the conditions for maximum copper loading. The capacity of this ligand exchanger for ammonia at various pH's was measured. The effect of temperature and time on steam regeneration of the exhausted exchanger was obtained. The effect of specific inorganic ions on the process and the effect of organics on the ligand exchange process with steam regeneration was investigated. Exchange capacity after repeated loading and recycling was measured. Finally, the process performance was demonstrated using lime clarified, secondary municipal effluent.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| *Ligands<br>*Ammonia<br>*Ion exchangers | Hydrous zirconium oxide<br>Wastewater treatment | 13B |

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U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

PRICES SUBJECT TO CHANGE

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS (This Report) | 21. NO. OF PAGES |
|---|---|---|
| RELEASE TO PUBLIC | UNCLASSIFIED | 77 |
| | 20. SECURITY CLASS (This page) | 22. PRICE |
| | UNCLASSIFIED | 5.00 - 2.25 |

EPA Form 2220-1 (9-73)

100054

EPA-600/2-76-103
April 1976

PB251418

# AMMONIA REMOVAL FROM WASTEWATER BY LIGAND EXCHANGE

Final Report

by

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Contract No. 68-03-0455

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## ABSTRACT

The use of a ligand exchange process to remove ammonia from secondary treated municipal wastewater was examined in a laboratory study. A ligand exchanger consisting of copper ions retained on a hydrous zirconium oxide ion exchanger was examined. Its ability to remove ammonia and subsequent regeneration with low pressure steam was evaluated. The main objective of the program was to optimize the conditions to achieve maximum efficiency and to determine the effect of other wastewater constituents on the process.

Initially, the capacity of the hydrous zirconium oxide for copper was examined to determine the conditions for maximum copper loading. The capacity of this ligand exchanger for ammonia at various pH's was measured. The effect of temperature and time on steam regeneration of the exhausted exchanger was obtained. The effect of specific inorganic ions on the process and the effect of organics on the ligand exchange process with steam regeneration was investigated. Exchange capacity after repeated loading and recycling was measured. Finally, the process performance was demonstrated using lime clarified, secondary municipal effluent.

This report was submitted in fulfillment of Contract Number 68-03-0455 by Gillette Research Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of March 1975.

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## ACKNOWLEDGEMENTS

Helpful discussions on the technical aspects of this work with Professor George Nancollas, State University of New York at Buffalo, is gratefully acknowledged.

The assistance of Dr. Richard Dobbs, EPA-MERL, Cincinnati, Ohio on the practical aspects of wastewater treatment is also acknowledged as well as the interesting discussions on the technical aspects of ligand exchange. His loan of a fraction collector and his aid in obtaining total organic carbon analyses and wastewater samples were invaluable.

# SECTION I

## CONCLUSIONS

The concept of ligand exchange has been applied to municipal wastewater treatment for removal of ammonia from secondary treated effluent. The use of cupric ion on a hydrous zirconium oxide ion exchanger was found to remove ammonia from solution, with low pressure steam being an acceptable regenerant.

Maximum copper loading onto the hydrous zirconium oxide occurs at high pH, with the solution made alkaline with ammonium hydroxide. Values in the range 0.6-0.7 mmoles copper/gm exchanger were obtained in the pH range of 11 to 12.

Steam regeneration was temperature dependent, with maximum regeneration complete after four column volumes of condensed steam at 135°C.

Maximum ammonia uptake by the ligand exchanger occurred at pH 10 to 11 and corresponded to 0.1 mmole ammonia/mmole copper. Therefore, the copper was not fully utilized, either because it was tightly bound to the ion exchanger or not available for ammonia coordination.

Repeated loading and regeneration through 25 cycles showed no physical particle breakdown nor copper leaching, though some ammonia capacity was lost. Common inorganics and organics had minimal effect on the overall process.

Use of secondary treated wastewater through five cycles was successful, with the exchanger capacity being near that for pure ammonium chloride solution, and essentially no loss of capacity being indicated through the five cycles.

## SECTION II

## RECOMMENDATIONS

This project was limited to a laboratory study of the use of copper loaded-hydrous zirconium oxide in removing ammonia from municipal wastewater and steam regeneration of the exchanger. The use of pure solutions permitted the collection of data to obtain information on the value of ligand exchange for wastewater treatment. Optimization of some of the operational variables, repeated loading experiments, and repeated cycling with lime-clarified, secondary municipal effluent showed that the wastewater results were consistent with results using pure solutions. Especially from the results of repeated loading experiments, it is recommended that pilot tests be carried out to determine the long term chemical stability of the ligand exchange process.

It should be noted, however, that the capacity of the ligand exchanger for ammonia was low (0.1 mmole ammonia/millimole copper) and needs to be improved. Knowledge of the ammonia content of the exchanger after copper loading and regeneration would aid in determining methods of increasing ammonia capacity. This could be accomplished by such methods as: re-evaluating the regeneration process to remove more ammonia from the loaded exchanger; using an inert support for the hydrous zirconium oxide to allow more surface contacts or examining different ion exchangers to determine if copper loading can be significantly increased. Further laboratory studies of these solutions are recommended.

## SECTION III

## INTRODUCTION

High demands are being placed on the nation's fresh water resources. Due to population location and fresh water distribution, there are parts of the country that face acute clean water shortages. Some cities are using water from streams and rivers that are dumping grounds for the effluent of cities and towns upstream from it. There is also the problem of eutrophication caused by nutrients being discharged as an integral part of the wastewater effluent.

Wastewater can be made suitable for reuse by complete treatment.[1] However, complete treatment of wastewater is a multi-step operation.[2] Conventional primary and secondary treatment of municipal wastewater still leaves large amounts of pollutants in the discharge. For example, in 1966 about 1.2 billion pounds of total nitrogen were discharged into U. S. streams from municipal outfalls.[3] Generally, effluent from secondary treatment contains about 20 mg/l ammonia.

The desire to remove ammonia from municipal wastewater is high: (1) Ammonia is oxidized to nitrite ion in natural water systems. As such, it consumes oxygen in the receiving water. Over 60 percent of the biological oxygen demand from the effluent of a municipal treatment plant can be due to the oxidation of ammonia;[4] (2) Ammonia is a plant nutrient and aids in inducing algal growth; (3) It reacts with chlorine to form chloramines, which are poorer disinfectants than chlorine. Also, the toxicity of the chloramines has recently been questioned; (4) Ammonia is corrosive to certain metal alloys of copper and zinc. Due to

the fact that nitrate ion is also a plant nutrient, the removal of ammonia from municipal wastewater rather than just oxidizing it becomes necessary.

At present, at least four treatment methods have been used to remove ammonia at municipal treatment plants.[5-10] These methods are: biological nitrification-denitrification, air-stripping, ion exchange using the natural zeolite, clinoptilolite, and breakpoint chlorination. Each of these methods has its advantages as well as disadvantages. The biological process is sensitive to pH, temperature, shock loading and destruction of the bacteria colony by certain toxic components in the wastewater. Air-stripping is temperature dependent, being inefficient in cold weather, causing fogging and icing in the vicinity at lower temperatures and the towers are affected by calcium deposits. Ion exchange is hampered by the selectivity of the clinoptilolite for ammonium ion for the other cations in wastewater. Breakpoint chlorination increases the dissolved solids in the effluent.

The new physical-chemical process examined in this study utilizes the concept of ligand exchange.[11] Ligand exchange exploits the ability of certain metal ions, especially the transition metal ions, to form complexes with molecules and ions that contain an unshared pair of electrons. The ligand exchanger is prepared by retaining the reactive metal ion on a suitable ion exchange material. Then the free, coordinated water molecules attached to the metal ion will be available to react with perspective molecules or ions (ligands). In aqueous solution the reaction

$$M(H_2O)_x^{n+} + yL \rightleftarrows M(H_2O)_{x-y}L_y^{n+} + yH_2O \qquad (1)$$

can occur where M is the metal ion of charge +n, and coordination number x, L is a neutrally charged ligand, and y is an integer between zero and x, depending on the stability of the system. In a ligand exchange system, the metal ion, M, will be sorbed on the ion exchanger, and the ligand, L,

will be able to replace the available coordinated water molecules attached to M. Thus, it can be seen that one of the advantages of utilizing the ligand exchange process in wastewater purification is that no new species are added into the effluent.

In order for the ligand exchange process to be successful for ammonia removal from municipal wastewater, certain criteria must be met. The metal ion must be selective for ammonia, it must be labile (reaction complete in a few seconds), and it must be strongly held on the ion exchanger so that metal bleed and loss of capacity does not occur and a suitable regeneration process must be available.

The stability constants for a number of metal complexes have been reported.[12] Examination of the data shows that ammonia forms the most stable complexes with cobalt (III) and copper (II). However, while copper (II) complexes undergo substitution reactions quite rapidly and is thus classified as being labile, cobalt (III) complexes are extremely inert with regards to substitution and have extremely low rate constants.[13, 14] Therefore, the logical choice would be to use copper as the metal ion. In aqueous solutions, for the reaction*

$$Cu(NH_3)^{2+}_{n-1} + NH_3 \rightleftarrows Cu(NH_3)^{2+}_{n} \qquad (2)$$

and a stability constant, $K_n$, defined as

$$K_n = \frac{[Cu(NH_3)^{2+}_n]}{[Cu(NH_3)^{2+}_{n-}]\,[NH_3]} \qquad (3)$$

the values of $K_n$ at 25°C and an ionic strength of 2$\underline{M}$ are $10^{4.3}$, $10^{3.6}$, $10^{3.0}$ and $10^{2.2}$ $\underline{M}^{-1}$ for n = 1,2,3 and 4 respectively.

---

* Water molecules have been omitted for clarity.

In evaluating various ion exchangers, Dobbs[15] found that chelating resins, strong-acid cation exchangers and weak-acid cation exchangers were unacceptable due either to low capacity or excessive metal bleed. Ion exchange columns prepared with hydrous zirconium oxide has been reported[16,17] to be used in adsorbing copper-ammine complexes from solution. Since this is the end product that would be expected from removal of ammonia with copper, attention was turned towards it. A great deal of information is known about inorganic ion exchangers[18, 19] and hydrous zirconium oxide in particular.[20, 21] Hydrous zirconium oxide can be prepared by neutralizing a solution of zirconyl chloride. The gel-like mass formed can be dried to various states of hydration, $ZrO_2 \cdot nH_2O$. However, no actual discreet hydrates have been identified, giving rise to the term hydrous zirconia. It is felt that the water is adsorbed onto the surface of the zirconium dioxide skelton. Other substances can also be adsorbed onto the hydrous zirconium oxide,[22] including copper ions.

The amphoteric hydrous oxides can act as either anion or cation exchangers, depending on the pH of the solution. This type of behavior of hydrous zirconium oxide has been studied by Kraus et al.[21] who determined exchange capacity of the oxide for both sodium ion as the cation, and chloride ion as the anion. Their material had a cation capacity of 0.1 mmoles/g at pH 6.5 which increased to about 0.4 mmoles/g at pH 10.5.

In relation to the ligand exchange process under evaluation, the following reactions would be involved.

$$\overline{2R^-} + Cu(H_2O)_4^{2+} \rightleftarrows \overline{(R^-)_2Cu(H_2O)_4^{2+}} \qquad (4)$$

$$\overline{2R^-} + Cu(NH_3)_4^{2+} \rightleftarrows \overline{(R^-)_2Cu(NH_3)_4^{2+}} \qquad (5)$$

$$\overline{(R^-)_2Cu(H_2O)_4} + 4NH_3 \rightleftarrows \overline{(R^-)_2Cu}\,\overline{(NH_3)_4^{2+}} + 4H_2O \qquad (6)$$

where $R^-$ refers to the fixed exchange groups on the hydrous zirconium

oxide and the bar refers to the solid exchanger phase. Equations 4 and 5 refer to the retention of aquated cupric ions and the tetraammonium copper (II) complex, respectively, by the ion exchanger. These are the general reactions that would take place in forming the ligand exchanger. Equation 6 is a general representation of the exchange process. The forward reaction describes the removal of ammonia from solution while the reverse reaction signifies a method of regeneration of the exchanger.

To determine the theoretical capacity of such a process for ammonia removal based on an equilibrium concept, consider the simple reaction

$$\overline{(R^-)_2Cu(H_2O)_4^{2+}} + NH_3 \rightleftarrows \overline{(R^-)_2Cu(H_2O)_3NH_3^{2+}} + H_2O \quad (7)$$

The equilibrium expression for this reaction is:

$$K_E = \frac{[\overline{(R^-)_2Cu(H_2O)_3NH_3^{2+}}]}{[\overline{(R^-)_2Cu(H_2O)_4^{2+}}]\,[NH_3]} \quad (8)$$

where $K_E$ is the equilibrium constant. In solution. ammonia is in equilibrium with ammonium ions. This is described by

$$NH_3 + H^+ \rightleftarrows NH_4^+ \quad (9)$$

and

$$K_H = \frac{[NH_4^+]}{[NH_3]\,[H^+]} \quad (10)$$

Since the total ammonia concentration is the sum of the ammonia and the ammonium ion,

$$[NH_3]_T = [NH_3] + [NH_4^+] \quad (11)$$

equations 10 and 11 can be combined and substituted into equation 8 to yield

$$K_E = \frac{\overline{[(R^-)_2Cu(H_2O)_3NH_3^{2+}]}\ (1 + K_H\,[H^+])}{\overline{[(R^-)_2Cu(H_2O)_4^{2+}]}\ [NH_3]_T} \qquad (12)$$

Knowledge of these various terms would allow the calculation of $K_E$. As a first approximation, it would not be expected to be greatly different from the value of $K_1$, the equilibrium constant for the reaction in aqueous solution (equation 3).

The aim of the project presented in this report was to determine if this concept could be applied to a wastewater system. Variables of interest are: maximum copper loading of the hydrous zirconium oxide; effect of pH of feed water on ligand exchange capacity; effect of specific inorganic ions on the process; effect of organics on the process; the ability to regenerate spent exchanger using low pressure steam; the effect of repeated loading and regeneration cycles on exchange capacity. Once these variables were studied a demonstration was needed that the process works using actual pretreated municipal wastewater.

## SECTION IV

## EXPERIMENTAL

### MATERIALS

#### Water

Ammonia free water was generated by passing single distilled water through a mixed bed strong acid-strong base ion exchanger, Rexyn® I-300. This water was prepared as needed for sample dilution, reagent blanks in ammonia analysis, column backwashing and as a final rinse for all glassware that would be in contact with the ammonia solutions.

#### Hydrous Zirconium Oxide (HZO)

Bio-Rad HZO-1 ion exchange crystals of only one lot were used in this study. The crystals were 20-50 mesh size and had a listed capacity as $Cr_2O_7$ at pH 1 of 1.5 meq/gm and 2.1 meq/ml of settled bed.

#### Reagents

All chemicals used for experimental or analytical purposes were reagent grade or purer.

### PROCEDURES

#### Ligand Exchanger Pretreatment

Before use or analytical evaluation, the copper loaded HZO was dried in a constant temperature-humidity room at 20.1°C (70°F) and 65 percent relative humidity to a constant weight.

## Batch Experiments

In a typical batch experiment, the bath solution was prepared, adjusted to the proper pH and placed in an Erlenmeyer flask. Then a weighed amount of the ligand exchanger was placed in the flask, which was then shaken, either on a Burrell shaker or by hand, for 10 minutes. The flasks were allowed to stand at least overnight with additional, occasional shaking, before aliquots were removed from the solution for chemical analysis.

## Column Operation

In all experiments where solutions were run through exchange columns, the same general technique was used. A weighed amount of exchanger was placed in a specially adapted Chromaflex* column. (These columns had been constricted at the top to allow the use of a Swagelok fitting when necessary for steam treatment. They were also coated externally to reduce the chance of flying glass, should they happen to shatter when under steam pressure). The loaded column was then back-washed twice with boiling, ammonia-free water to remove trapped air. To keep the rate of solution feed constant, a Masterflex+ pump was used. The test solution was pumped through silicone rubber tubing into the stoppered column, using a hypodermic syringe. The eluate was fractionated automatically, using either a Buchler Fraction Collector or an SMI Model 12063 fraction collector, depending on the size of the fractions taken. Since most runs were planned to be completed in one overnight operation, sulfuric acid was added to each of the collection vessels to minimize volatile loss of ammonia.

## Steam Regeneration

A Chromalox Model CMB-42 electric steam boiler was connected to a Watts Model 206 steam regulator to provide a controllable pressure steam

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* A trademark of TM Kontes Glass Co.

\+ A trademark of Cole-Parmer Co.

source in the range of 137.9-310.3 kilopascals (gauge) (20-45 psi g.). A schematic diagram of the regeneration apparatus is shown in Figure 1. Steam generated by the boiler passed through the regulating valve and into the copper tubing. All tubing was wrapped with asbestos tape to minimize cooling effects. In the line were a pressure gauge and water vent before the final t-shaped, Swagelok fitting. This allowed for the placement of a thermocouple at the head of the column to monitor the steam temperature.

Experimentally, the exchange column was drained and attached to the generator utilizing a Swagelok fitting. To the column exit was attached a water-cooled condensor. With the drainage valve open, the steam generator was turned on and brought up to pressure. The boiler valve was then opened and the steam was allowed to run until all the condensed water was removed from the system. The valve protecting the column was then opened and the drainage valve shut, allowing the steam to pass through the column.

Ammonia Analysis

Ammonia analysis was performed in accordance with the automated phenolate method for total nitrogen.[23] This is a variation of the indophenol blue test where ammonia reacts with hypochlorite ion to give chloramine, which in turn couples with phenol to give indophenol. A test solution aliquot (10.0 ml for standards, 2.0 ml for samples) was placed in a 25 ml volumetric flask. The acidified column fractions were neutralized with 2M NaOH. Then sodium phenolate, sodium nitroprusside and sodium hypochlorite solutions were added in that specific order and then diluted to volume. The flask was placed in a water bath at 36°C for 30 minutes. After the flask was removed from the water bath and cooled to room temperature, the absorbance of the solution was read at 640 nm against a reagent blank. Ammonium sulfate was used to construct the standard curve, which was determined each day that analyses were performed.

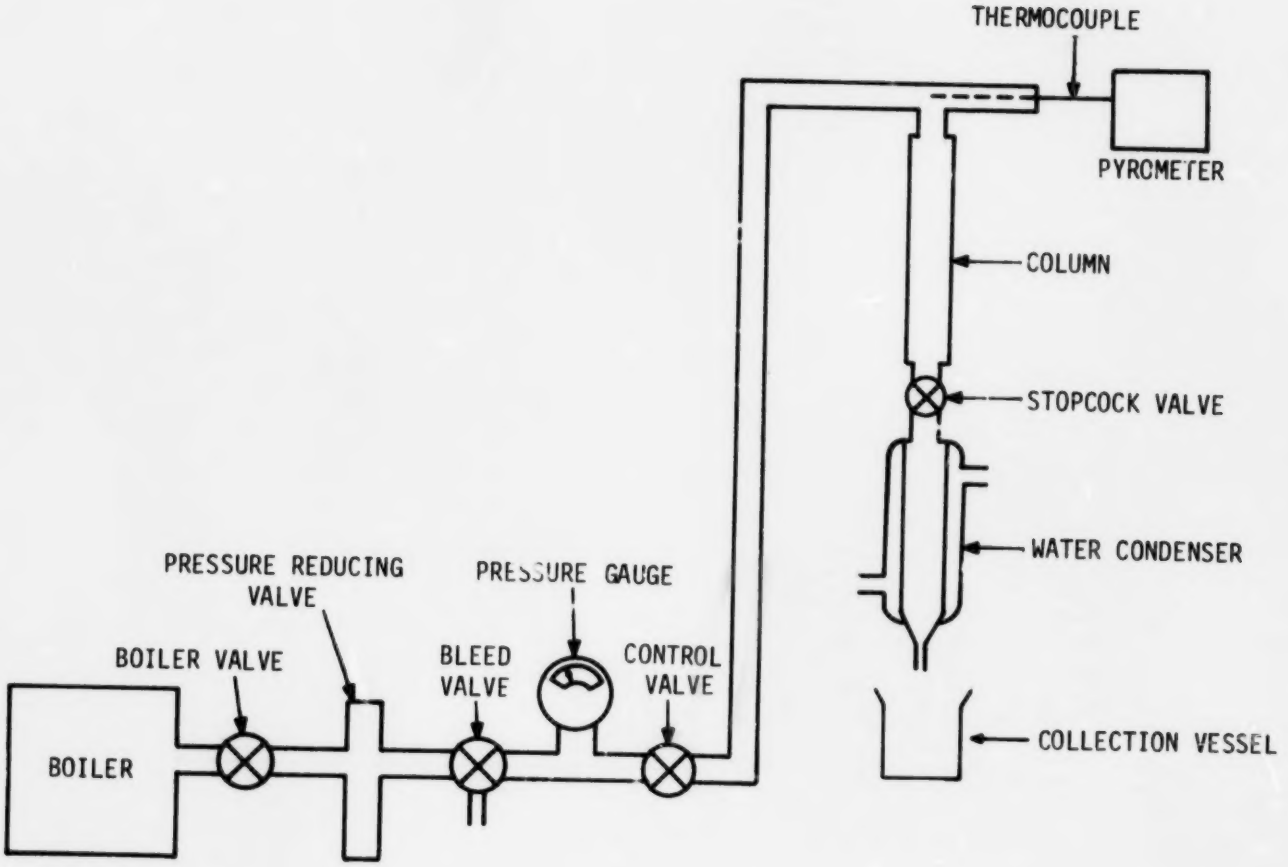


Figure 1. Schematic diagram of the steam regeneration process.

When calculating the ammonia concentrations, a regression analysis was performed using a standard computer program to determine the best straight line for the standard curve. (All work was performed in a concentration range where Beer's Law was obeyed.) Then the experimental points, as well as dilution data, were fed into the computer, which calculated the ammonia concentrations in the unknown.

Copper Analysis

Copper present in eluate samples was measured with a Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer. Analyses were performed both with the burner and, in certain cases, with the graphite furnace. For analysis of copper on the hydrous zirconium oxide ion exchanger, elution techniques were found to be inadequate. Therefore, a weighed sample of the exchanger was placed in a beaker, covered with water and treated with small additions of concentrated hydrocholoric acid. After the bubbling and effervescence subsided, the beaker was placed on a hot plate and the solution warmed until dissolution had occurred. After cooling, this solution was transferred to a volumetric flask and diluted with 0.1 M nitric acid. Copper was then measured by atomic absorption techniques.

For concentrated solutions of copper salts in an excess of ammonium hydroxide, the absorbance of the tetraaminecopper(II) ion at 610 nm was used for analytical determination. Beer's Law was obeyed in the concentration range of 0.001 M to 0.02 M.

Fluoride Analysis

Fluoride ion was measured using an Orion fluoride sensitive electrode.

Total Organic Carbon

Total organic carbon analyses were performed at the National Environmental Research Center, Cincinnati, Ohio, using a Beckman Model 915 Total Carbon Analyzer.

## SECTION V

## RESULTS AND DISCUSSION

### COPPER LOADING ON HYDROUS ZIRCONIUM OXIDE

The necessary first step of the study was to optimize the conditions for obtaining maximum copper uptake on the HZO. Two methods were examined: 1) converting the HZO ion exchanger to the sodium form and 2) increasing the pH of the copper containing solution as much as possible. Initial experiments along these lines were performed and the data are presented in Table 1. Experimentally, columns containing HZO were dynamically loaded with the reported copper containing feed solutions. The effluents were collected in fractions, made 1M in ammonium hydroxide and analyzed spectrophotometrically for copper. The total uptake was estimated by numerically integrating the copper breakthrough curve. Certain columns were converted to the sodium form by passing 150 ml of 1.0 M sodium hydroxide through it, followed by washing with large amounts (~ 6 liters) of distilled water to bring the pH back to neutrality. A cupric chloride solution was then passed through one column. After about 150 ml of feed the column clogged. Examination of the column indicated that copper hydroxide must have precipitated in the column. Therefore, the calculated uptake of 0.23 mmoles Cu/g HZO was not all sorbed on the exchanger. This method was abandoned.

Using the other method of attempting to take advantage of the increased cation exchange capacity of HZO at high pH, the cupric chloride feed solution was made 1.0 M in ammonium hydroxide. Under these conditions the predominant species in solution was the tetraaminecopper(II) complex. A substantial increase in copper uptake was noted under these conditions

relative to the lower pH. However, no difference was noted due to the form of the HZO exchanger. The capacity of 0.59 mmoles Cu(II)/g HZO compares favorably with the data reported by Kraus et al,[21] being higher than the last point reported by them at pH 10. This would also indicate that the ion exchange process found with sodium ion by the above authors was also operative for the tetraaminecopper(II) complex.

Table 1. COPPER UPTAKE ON HZO

| Item | Column No.[a] | | | |
|---|---|---|---|---|
| | 1 | | 3 | 4 |
| Weight of HZO-g | 44.2 | 41.5 | 44.0 | 40.4 |
| Initial form | as received | $Na^+$ | as received | $Na^+$ |
| Feed solution 0.1 M $CuCl_2.2H_2O$ | Dist. water | Dist. water | 1.0 M $NH_4OH$ | 1.0 M $NH_4OH$ |
| pH | 4.3 | 4.3 | 11.5 | 11.5 |
| Volume throughput-l | 0.30 | 0.15[b] | 0.32 | 0.32 |
| Flow rate, ml/min | 10.0 | 7.0 | 7.0 | 7.0 |
| Copper uptake (millimoles/gm) | 0.11 | 0.23 | 0.57 | 0.59 |

[a] 1.27 x 20 cm columns.
[b] Column clogged after 150 ml of feed had passed.

To further increase the capacity of the resin for copper by increasing pH, a series of experiments were performed where the pH was adjusted with sodium hydroxide. A feed solution was prepared that contained 0.1 M $CuCl_2$ and 0.5 M $(NH_3)_2SO_4$ (in order to form the copper-ammonia complex) and adjusted to the experimental pH using 10 M NaOH. The copper content was determined by sacrificing some of the exchanger and analyzing it for copper. Experimentally, after loading of the column had been completed (when the absorbance of the effluent at 610 nm was the same as the

feed solution) it was washed with 1 M $NH_4OH$ and finally with distilled water. It was found that the $NH_4OH$ solutions was necessary to prevent precipitation in the column. The exchanger was then dried to constant weight and a sample then taken for analysis. Table 2 presents the data obtained. As can be seen, there was a maximum in the uptake at around pH 10. However, by adjusting the pH with sodium hydroxide the sodium ion concentration was also increased. Therefore there might be competition of sodium ion and tetraaminecopper(II) for the HZO exchanger.

Table 2. EFFECT OF pH ON COPPER UPTAKE USING NaOH

| | Feed pH | | | | |
|---|---|---|---|---|---|
| | 8.5 | 9.0 | 10.0 | 11.4 | 12.5 |
| Wt. HZO, g | 8.59 | 8.59 | 8.58 | 8.32 | 8.69 |
| Cu found, mg | 41.25 | 77.08 | 127.00 | 90.50 | 61.00 |
| g Cu/g HZO | 4.80 | 8.98 | 14.80 | 10.88 | 7.02 |
| mmole Cu/g HZO | 0.076 | 0.14 | 0.23 | 0.17 | 0.11 |

To further elucidate the role that sodium ions might be exhibiting on the system, a series of batch experiments was performed where 4 M $NH_4OH$ was used. Then the pH need only be adjusted with hydrochloric acid. The solutions were contacted with HZO for up to 28 days, with no difference noted in the measurements between this time period and just overnight equilibration. The copper retained by the exchanger was measured by isolating the copper loaded HZO, dissolving a weighed amount in hydrochloric acid and analyzing for copper by atomic absorption spectrophotometry. The results presented in Table 3 indicated that copper retention did increase with pH throughout the range examined and did not decrease at pH values greater than 11. This would indicate that sodium ion does compete with copper ion for the ion exchange sites on the hydrous zirconium oxide.

Table 3. EFFECT OF pH ON COPPER UPTAKE

| pH | 9.0 | 10.0 | 11.0 | 11.9 |
|---|---|---|---|---|
| Wt. HZO, g | 100 | 100 | 100 | 100 |
| Bath vol., ml | 1000 | 1000 | 1000 | 1000 |
| $[Cu(II)]^a$, M | 0.2 | 0.2 | 0.2 | 0.2 |
| $[NH_4^+]^a$, M | 4 | 4 | 4 | 4 |
| Contact time (days) | 28 | 28 | 28 | 28 |
| $Cu^{2+}$ uptake, mmol $Cu^{2+}$/g HZO | 0.20 | 0.39 | 0.51 | 0.59 |

[a] Initial concentration.

At this point, the remaining HZO in our possession was converted to the copper form by loading it dynamically using a 0.25 M cupric chloride solution in 4 M ammonium hydroxide. The exchanger was analyzed and found to contain 0.69 mmole Cu/g HZO.

STEAM REGENERATION

The success of an exchange process depends largely on a convenient, economic regeneration process. For a ligand exchange reaction, coordinated water molecules on the sorbed metal ions are replaced by another species. Regeneration would require removal of the new ligand and replacement by water. One possible method of regeneration for the copper-ammonia system under examination would be to use acid. This would release the coordinated ammonia in the form of ammonium ion. However in acid solution HZO is an anion exchanger and loss of copper would occur.

One possible method of regeneration that seems appealing is steam regeneration. It has the advantage that no contaminant or extraneous chemical species are added to the system. Therefore the complete

operation of the ligand exchange-regeneration process would consist essentially of forming a concentrated ammonia solution from a dilute one (the wastewater). The concentrated ammonia solution could then conceivably be put to practical use. Ammonia lends itself to steam regeneration. Being a gas, the equilibrium between the liquid and gas phases is temperature dependent. Therefore, by raising the water temperature, the ammonia can be distilled off the column.

A bench size, low pressure steam generator was used throughout the experimental program. The house steam lines were not used since long chain amines are added to the lines as a rust preventative and it was felt that this might adversely affect the column operation during subsequent loading steps. The actual set-up and operation of the regeneration process have already been presented in the experimental section.

Since the ligand exchangers were prepared from copper-ammonium hydroxide solutions, regeneration was necessary before a column could be loaded. In the first regeneration experiment, a column containing 40 grams of exchanger with 0.59 mmole Cu/g HZO was regenerated at 31.0 kPa (30 psig) which was also 135°C. The $NH_3$-N analyses for each column volume (one column volume = 24.9 ml) are shown in Table 4 and plotted in figures 2 and 3. In all, a total of 123.0 mg $NH_3$-N were removed, or 0.37 mmole $NH_3$/mmole Cu. Figure 3 shows that there was essentially an exponential relationship between the ammonia concentration in each column volume and the column volume number. Therefore, long regeneration times would not provide any benefit. A very interesting point to note was the low $NH_3$/Cu ratio. When loading the HZO with the copper-ammonium hydroxide solution, the species present in solution was the $Cu(NH_3)_4^{2+}$ ion. However, this experiment indicated that less than one ammonia molecule per copper was removable. Therefore, either a large percentage of the copper complex was completely tied up in the exchanger or else the ammonia was tightly bound to the copper.

To examine the effect of steam temperature, a regeneration experiment was run at 241 kPa (20 psig) which gave a steam temperature of 126°C. The

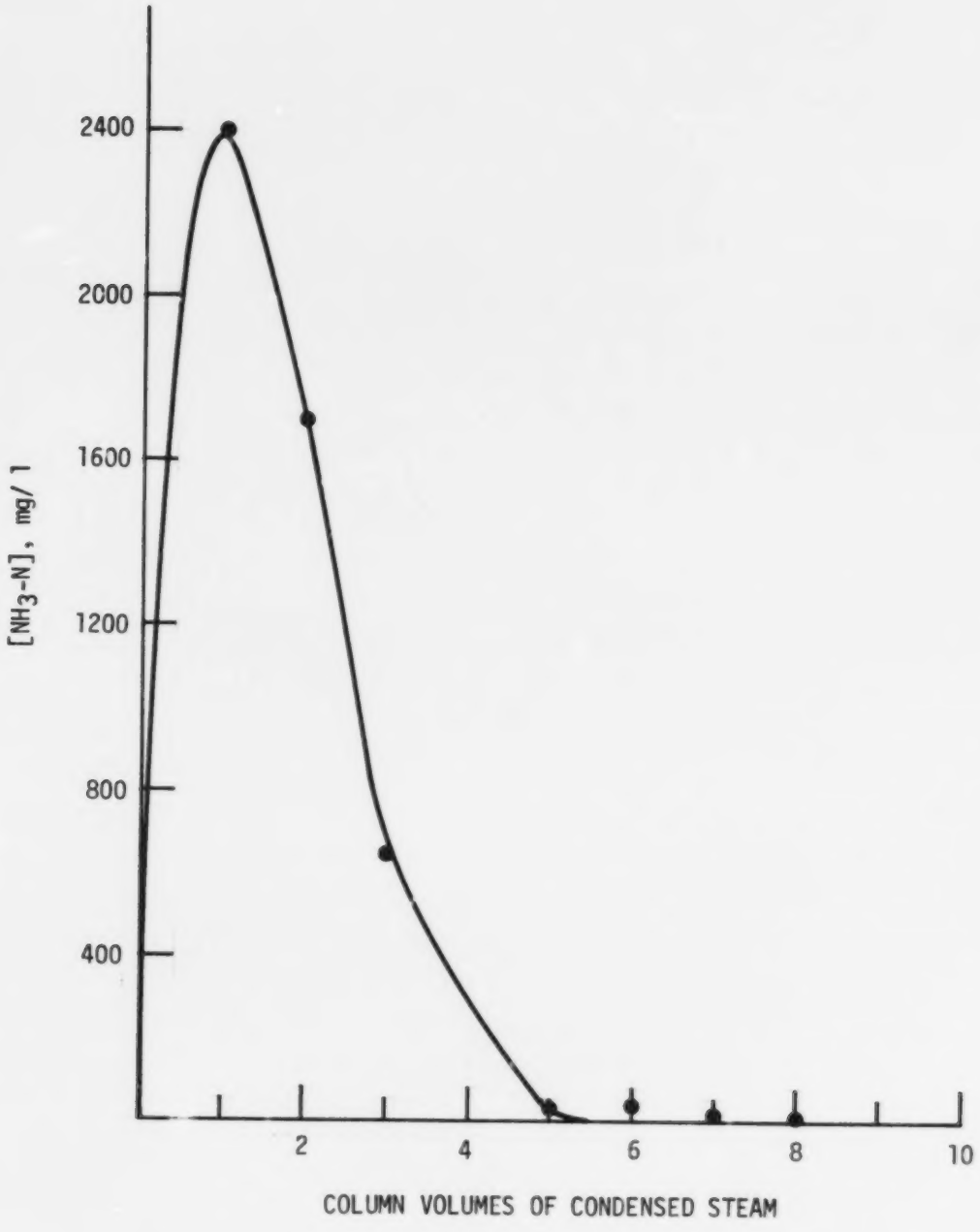


Figure 2. Steam regeneration at 135°C.

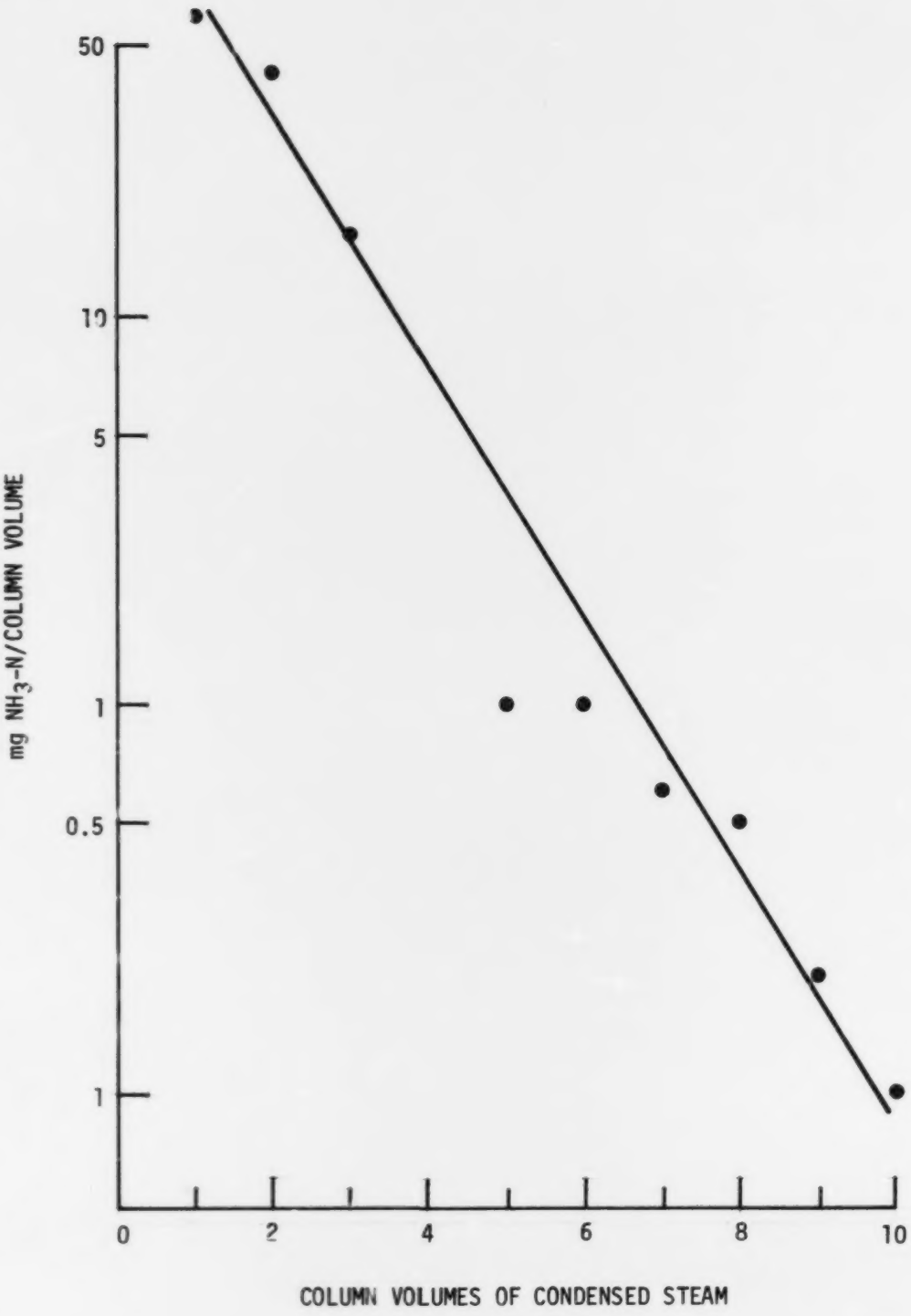


Figure 3. Ammonia Removal at 135°C.

Table 4. STEAM REGENERATION AT 135°C

| Column Volume[a] | Wt. $NH_3$-N, mg |
|---|---|
| 1 | 60 |
| 2 | 42.8 |
| 3 | 16.4 |
| 4 | 0.4 |
| 5 | 1.0 |
| 6 | 1.0 |
| 7 | 0.6 |
| 8 | 0.5 |
| 9 | 0.2 |
| 10 | 0.1 |

[a] one column = 24.9 ml.

column used was from a loading run and contained 45 gms of exchanger with a copper content of 0.31 mmole Cu/g HZO. The regeneration data are in Table 5 and plotted in Figure 4. A poor regeneration curve was obtained, due in part to the low levels of ammonia present in the fractions. However, from the loading data, only 2.3 mg $NH_3$-N were loaded on the column at breakthrough. Table 5 indicated that only 0.4 mg $NH_3$-N were recovered.

As for the temperature efficiency of steam regeneration, at 310 kPa (30 psig), 97 percent of the recoverable ammonia was obtained in four column volumes of condensed steam, while at 241 kPa (20 psig), only about 30 percent of the recoverable ammonia was obtained in the same four column volumes. Therefore steam pressure was quite important in regeneration

efficiency. Subsequent regenerations during this program were performed at 310 kPa (30 psig), with at least ten column volumes of condensate collected.

Table 5. STEAM REGENERATION AT 126°C

| Fraction[a] | Wt. $NH_3$-N, mg |
|---|---|
| 1 | 1.4 |
| 2 | 0.2 |
| 3 | 0.4 |
| 4 | 0.4 |
| 5 | 0.5 |
| 6 | 0.4 |
| 7 | 0.4 |
| 8 | 0.3 |
| 9 | 0.2 |
| 10 | 0.2 |

[a] Each fraction was 100 ml; one column volume = 25.3 ml.

OPTIMIZING pH FOR AMMONIA UPTAKE

In order for the ammonia to be removed it must be present as ammonia and not ammonium ion. For the simple reaction

$$(R^-)_2\,[Cu(H_2O)]^{++} + NH_3 \longrightarrow (R^-)_2\,[Cu(NH_3)]^{++} + H_2O \qquad (13)*$$

to occur, an unshared pair of electrons must be available on the ligand to share with the copper ion. Ammonium ion does not have this configuration

* Non-reacting, coordinated water molecules on the metal ion have been omitted for simplicity.

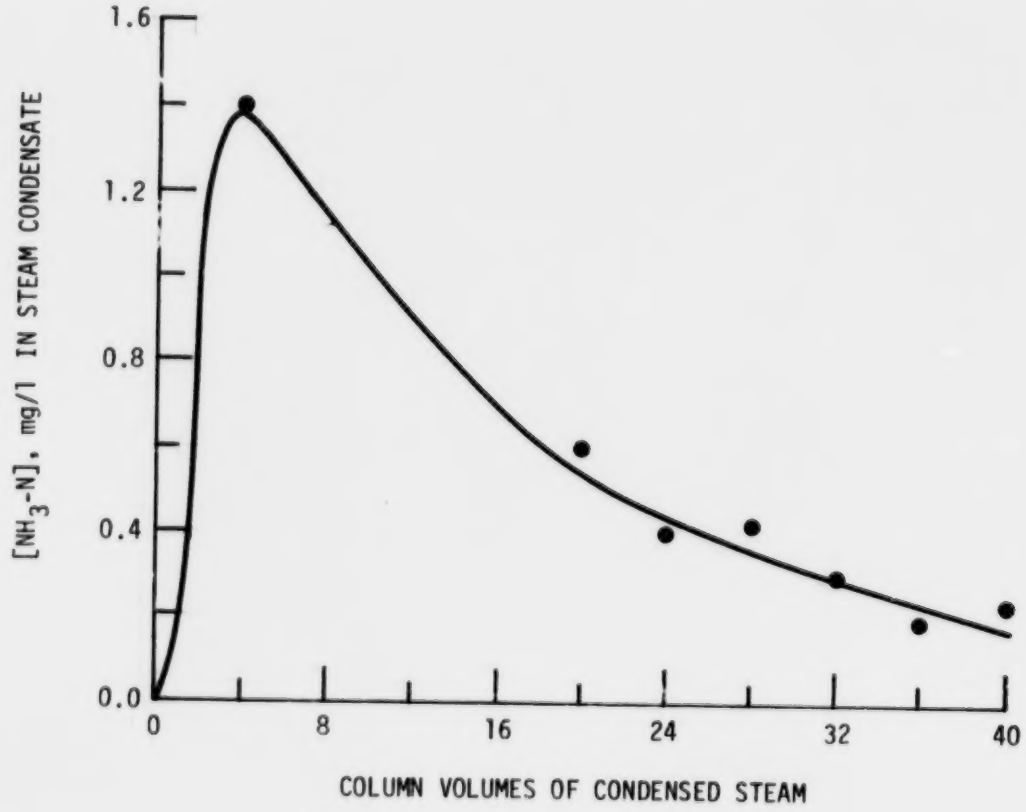


Figure 4. Steam regeneration at 126°C.

FIG 4

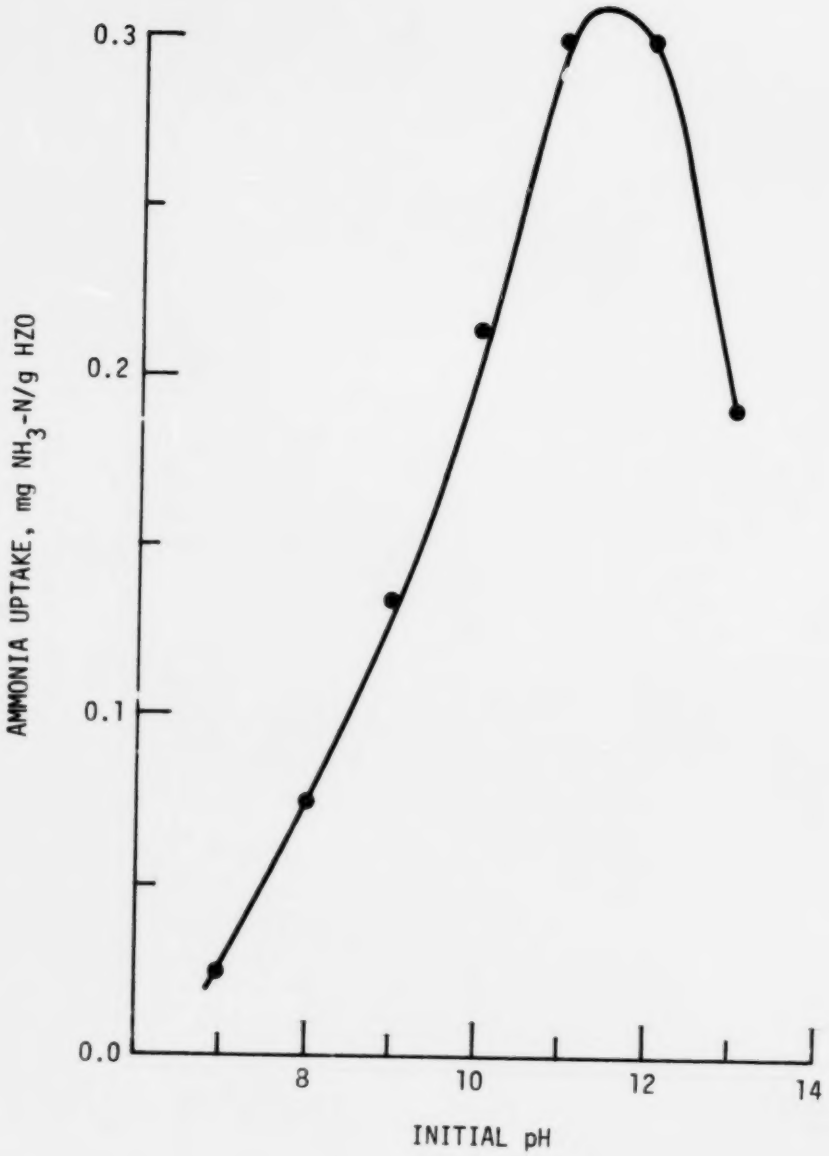


Figure 5. Ammonia uptake at varying pH.

and therefore is not reactive in this situation. The concentration of free ammonia in an aqueous solution of ammonium chloride is dependent on two factors, (1) the concentration of ammonium chloride and (2) the pH of the solution.

The weight of ammonium chloride will determine the total ammonia present. From a mass balance concept:

$$[NH_3]_T = [NH_3] + [NH_4^+] \tag{14}$$

where $[NH_3]_T$ is the total ammonia concentration. The ammonia and ammonium ion concentration are related by the equation:

$$K_H = \frac{[NH_4^+]}{[NH_3]\,[H^+]} = 3 \times 10^9\ M^{-1} \tag{15}$$

Solving these two equations for free ammonia gives:

$$[NH_3] = \frac{[NH_3]_T}{1 + K_H\,[H^+]} \tag{16}$$

For the simple reaction in equation 13 , that is, for each aquated copper ion picking up only one ammonia molecule, a new equilibrium constant, $K_E$, can be defined as

$$K_E = \frac{\overline{\overline{(R^-)_2\,[Cu(NH_3)^{2+}]}}}{\overline{\overline{(R^-)_2\,[Cu(H_2O)^{2+}]}}\,[NH_3]} \tag{17}$$

Substituting for free ammonia, the following is obtained:

$$K_E = \frac{\overline{\overline{(R^-)_2\,[Cu(NH_3)]^{2+}}}\,(1 + K_H[H^+])}{\overline{\overline{(R^-)_2\,[Cu(H_2O)^{2+}]}}\,[NH_3]_T} \tag{18}$$

Knowledge of the various concentrations would allow the calculation of $K_E$. However, from the steam regeneration data, it appeared that different complexes containing varying numbers of ammonia and water molecules might be present, e.g., $Cu(NH_3)_4^{2+}$, $Cu(NH_3)_3(H_2O)^{2+}$, $Cu(NH_3)_2(H_2O)_2^{2+}$, etc.

Therefore a more general equation must be used based on the reaction:

$$\overline{(R^-)_2 Cu(NH_3)_x(H_2O)_y^{2+}} + mNH_3 \rightleftarrows \overline{(R^-)_2 Cu(NH_3)_{x+m}(H_2O)_{y-m}^{2+}} + mH_2O \qquad (19)$$

where $x+y = 4$. The equilibrium expression, $K_m$, derived for this reaction and equations 15 and 16 would have the form

$$K_m = \frac{\overline{(R^-)_2 Cu(NH_3)_{x+m}(H_2O)_{y-m}^{2+}}\ (1 + K[H^+])^m}{\overline{(R^-)_2 Cu(NH_3)_x(H_2O)_y^{2+}}\ \left([NH_3]_T^m\right)} \qquad (20)$$

Batch Equilibrations

For the initial set of experiments aimed at determining the ammonia uptake, batch equilibrations were performed using two ammonia concentrations as well as two pH ranges. Two gram samples of copper loaded HZO (0.53 mmole Cu/g HZO) were placed in 100 ml of ammonium chloride solutions that had been previously adjusted to different pH's. For one set of runs at initial pH of 7.0, 8.0, 9.0, 10.0 and 11.0, an ammonium chloride solution containing 0.9 mg/l $NH_3$-N was used. For the other set, at initial pH's of 10.0, 11.0, 12.0 and 13.0, an ammonium chloride solution containing 0.25 mg/l $NH_3$-N was used. In these two sets of experiments, both the initial and final ammonium determinations were performed on aliquots of the solution.

The higher ammonia concentration runs shown in Table 6 indicated that maximum ammonia uptake occurred at a pH of approximately 10. It is interesting to note that 15.2 mg $NH_3$-N (approximately one mmole) removed by 2 gms of HZO loaded with 0.53 mmole of copper corresponds to only one

ammonia coordinated to each copper ion. For the higher [$NH_3$-N] series, maximum uptake was also near pH of 10, with subsequent increase in pH causing a decrease in ammonia removal.

Table 6. AMMONIA LOADING FROM BATCH EQUILIBRATIONS USING HIGH AMMONIA CONCENTRATIONS

| pH | | Wt. ammonia, mg $NH_3$-N | | Uptake | |
|---|---|---|---|---|---|
| Initial | Final | Initial | Final | $NH_3$-N, mg | $\frac{\text{mmole } NH_3}{\text{mmole Cu}}$ |
| 7.0 | 7.1 | 88.0 | 84.3 | 3.7 | 0.25 |
| 8.0 | 7.8 | 88.0 | 81.5 | 6.6 | 0.44 |
| 9.0 | 9.1 | 88.0 | 77.3 | 10.7 | 0.72 |
| 10.0 | 10.1 | 88.0 | 72.8 | 15.2 | 1.02 |
| 11.0 | 10.5 | 88.0 | 81.4 | 6.6 | 0.44 |
| 10.0 | 9.5 | 24.9 | 16.5 | 8.4 | 0.56 |
| 11.0 | 10.0 | 24.9 | 16.5 | 8.4 | 0.56 |
| 12.0 | 11.7 | 24.9 | 20.5 | 4.4 | 0.30 |
| 13.0 | 12.8 | 24.9 | 21.0 | 3.9 | 0.26 |

At a pH of 10 with a total ammonia concentration of 0.25 mg/l $NH_3$-N, only 0.1 gms/liter, or about 0.56 ammonia molecules per copper ion, of ammonia were removed. This indicated the equilibrium nature of the ligand exchange reaction under evaluation, with higher ammonia concentrations forming more of the copper-ammonia complex.

Determination of the equilibrium constant, $K_m$, could not be performed with these data, since the pH was seen to vary during the experiment. It was felt that the experiments necessary to determine the best m value to solve equation 20 would not be profitable at this time.

To gain information on ammonia removal that would be more applicable to a municipal wastewater situation, another set of experiments was performed covering an initial pH range from 7 to 12 using a solution containing a more realistic ammonia concentration, 16.5 mg/l $NH_3$-N. Again, two grams of exchanger were contacted with the prepared solution. After overnight equilibration in the stoppered flasks, aliquots were removed for quantitative determination of ammonia. Also, spot checks were performed on the liquid samples to determine if copper was released.

The results for these experiments are shown in Table 7 and plotted in Figure 5. The results indicated that the uptake of ammonia was pH dependent, increasing to a maximum in the pH range of 9-11 and then decreasing at the higher value. In most of the cases, the initial pH of the solution, before addition of the exchanger, was higher than the final pH measured. This was a consequence of the equilibrium between ammonia and ammonium ion (equation 9). At the lower pH values, where the ammonium ion species predominated, removal of ammonia caused an increase in the hydrogen ion concentration. Rapid equilibrium was achieved between ammonia and ammonium ion since the protolytic reactions are known to have high rate constants.[24]

Returning to the general expression for the simple case of removal of one ammonia molecule per copper ion, equation 7, and the equilibrium expression derived for it, equation 12, the portion of the pH-ammonia uptake curve between pH 7 and 10 can be explained. The lower the pH, the less free ammonia was present and hence the smaller the amount of ammonia removed. As the pH increased, more ammonia was removed. However, in the process of removing ammonia, protons were released which lowered the pH, causing the free ammonia concentration to be decreased even further.

At an initial pH of 11, the maximum uptake of ammonia was reached. This corresponded to a plateau where ammonia predominated over ammonium ion.

The uptake of 0.6 mg $NH_3$-N on 2 grams of HZO containing 1.2 mmole of copper corresponded to a molar ratio of 0.063 $NH_3$/Cu.

Table 7. BATCH EQUILIBRATION OF Cu-HZO WITH AMMONIA (16.5 mg/l $NH_3$-N)

| Bath pH | | Bath conc.[a] mg/l $NH_3$-N | | Wt. $NH_3$-N in bath, mg | | Exchanger uptake[b] | |
|---|---|---|---|---|---|---|---|
| Init. | Final | Init. | Final | Init. | Final | $NH_3$-N, mg | mmole $NH_3$ / mmole Cu |
| 7.0 | 7.05 | 16.5 | 15.40 | 0.825 | 0.77 | 0.055 | 0.003 |
| 8.0 | 7.20 | 16.5 | 13.50 | 0 825 | 0.675 | 0.150 | 0.009 |
| 9.0 | 7.60 | 16.5 | 11.10 | 0.825 | 0.555 | 0.270 | 0.016 |
| 10.0 | 7.95 | 16.5 | 7.88 | 0.825 | 0.394 | 0.431 | 0.026 |
| 11.0 | 8.65 | 16.5 | 4.50 | 0.825 | 0.225 | 0.600 | 0.036 |
| 12.0 | 11.10 | 16.5 | 4.50 | 0.825 | 0.225 | 0.600 | 0.036 |
| 13.0 | 13.10 | 16.5 | 8.87 | 0.825 | 0.444 | 0.381 | 0.023 |

[a] Volume of 50 ml.
[b] Exchanger was 2 grams containing 0.60 mmole Cu/g HZO.

At very high pH values, the uptake of ammonia decreased. This effect was also found in the second set of batch experiments, Table 6. At a pH of 13, the hydroxide concentration was 0.1 molar. Thus it is conceivable that with an ammonia concentration of $10^{-3}$ M, and $[OH^-]$ at $10^{-1}$ M, there was competition between these two species for the coordination sites on the copper.

Two conclusions could be drawn from these batch experiments: (1) The removal of ammonia was an equilibrium process, dependent upon the free ammonia concentration in the solution; and (2) maximum uptake of ammonia occurred at a pH of around 10 or 11, with possible uptake of $OH^-$ also occurring.

## Column Loadings

In conjunction with the batch experiments, column experiments were also run to determine optimum solution pH. Two columns were examined, one with a feed solution at pH 7, the other at pH 11. Glass columns of one-half inch dimension were filled with a weighed amount of copper-loaded HZO. Feed solutions of 16.5 mg/l $NH_3$-N were used. Figure 6 reports the results.

For the column with a feed solution at an initial pH of 7.3, a total of 2.3 mg $NH_3$-N were removed by 45 grams of exchanger which contained 0.31 mmole Cu/g HZO. This gave a ratio of mmole $NH_3$/mmole Cu of 0.012, which was in good agreement with the batch experiments. For the column at pH = 11.5, 24 mg $NH_3$-N were removed by 36.9 gms of exchanger which contained 0.59 mmole Cu/gm HZO. This corresponded to 0.079 mmole $NH_3$/ mmole Cu, or twice the amount from the batch experiments. Greater loading would be expected for dynamic loading as opposed to batch equilibration. In a batch equilibration the pH of the solution would be dependent on the equilibrium reaction. For column operation, fresh solution at the operating pH would counteract any pH changes due to proton formation, and would return the system to the operating pH. Also, in a batch experiment, depletion of ammonia occurs as the system approaches equilibrium. In a dynamic system, the bath concentration is always replenished.

## Repeated Loading

One condition necessary for satisfactory use of an exchanger is physical and chemical integrity of it through repeated loading and regeneration cycles. Initially, to determine this, two columns were put in operation. Table 8 lists the variables of the two columns. A feed pH of 10.0 was used since this was found to be the pH of maximum uptake. The liquid linear speed was varied by a factor of two. Figures 7 and 8 present the breakthrough curves for these columns. Highly irregular effluent concentration fluctuations were apparent in these curves. For column 1,

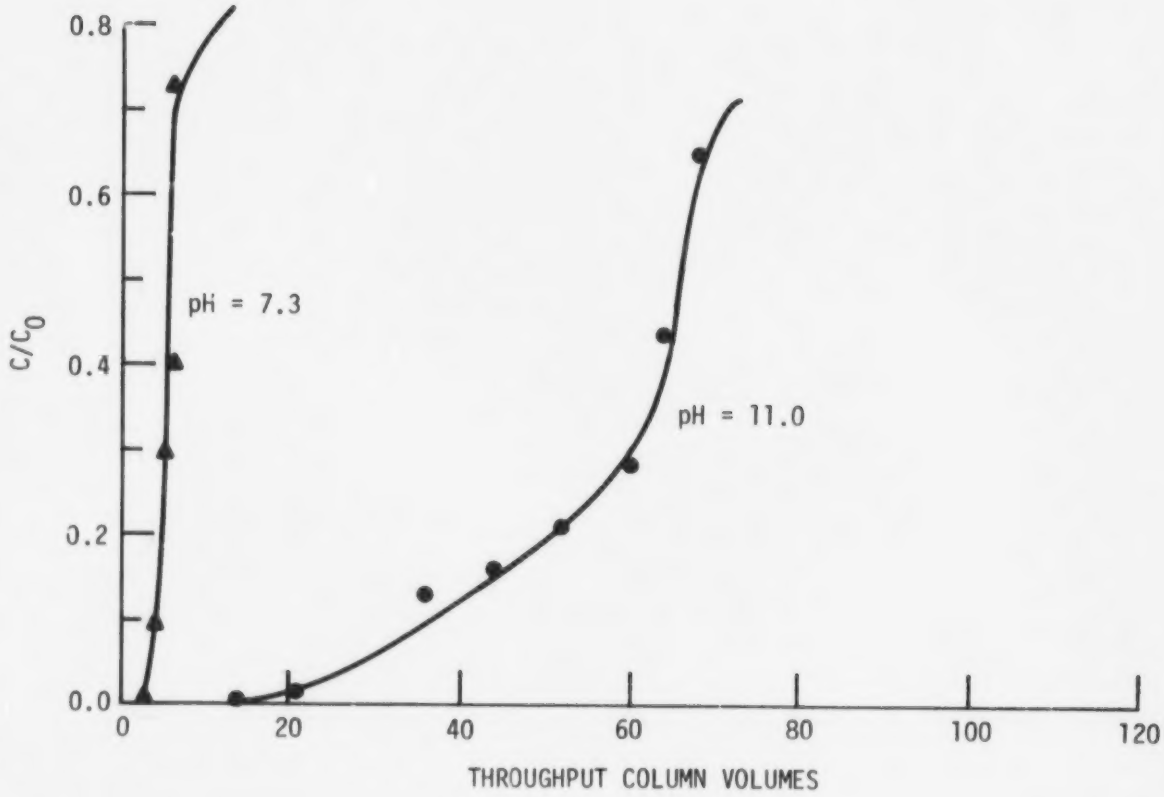


Figure 6. Ammonia breakthrough at pH 7 and 11.

FIG 6

the feed supply was interrupted for 12 hour intervals after 110, 220 and 330 column volumes had passed through. For column 2, an interruption of 12 hours duration occurred after 180 column volumes. It was seen that after each interruption, the ammonia concentration in the effluent decreased, indicating that additional ammonia had been removed during the period when the column was standing. One explanation for this phenomenon is that diffusion of the ammonia or ammonium ion into the HZO particle water is taking place. Here, either the ammonia binds to a copper ion that was previously unavailable, or else the ammonium ion was retained by the hydrous zirconium oxide, which acted as a cation exchanger at pH 10.

Table 8. EXPERIMENTAL CONDITIONS FOR REPEATED LOADING EXPERIMENTS

| Column | 1 | 2 |
|---|---|---|
| Feed, mg/l $NH_3$-N | 16.5 | 16.5 |
| Feed pH | 10 | 10 |
| Wt. exchanger, g | 55.2 | 25.0 |
| Exchanger mesh size | 20-50 | 20-50 |
| Col. diameter, cm | 1.27 | 1.27 |
| Col. length, cm | 26.7 | 11.7 |
| Col. volume, ml | 32 | 15 |
| Col. aspect ratio | 19.8 | 9.2 |
| Vol. flow rate, ml/min | 10 | 5 |
| Liquid linear speed, cm/min | 7.89 | 3.95 |
| Repetition cycle | 1 | 1 |
| mmole Cu/g HZO | 0.53 | 0.53 |

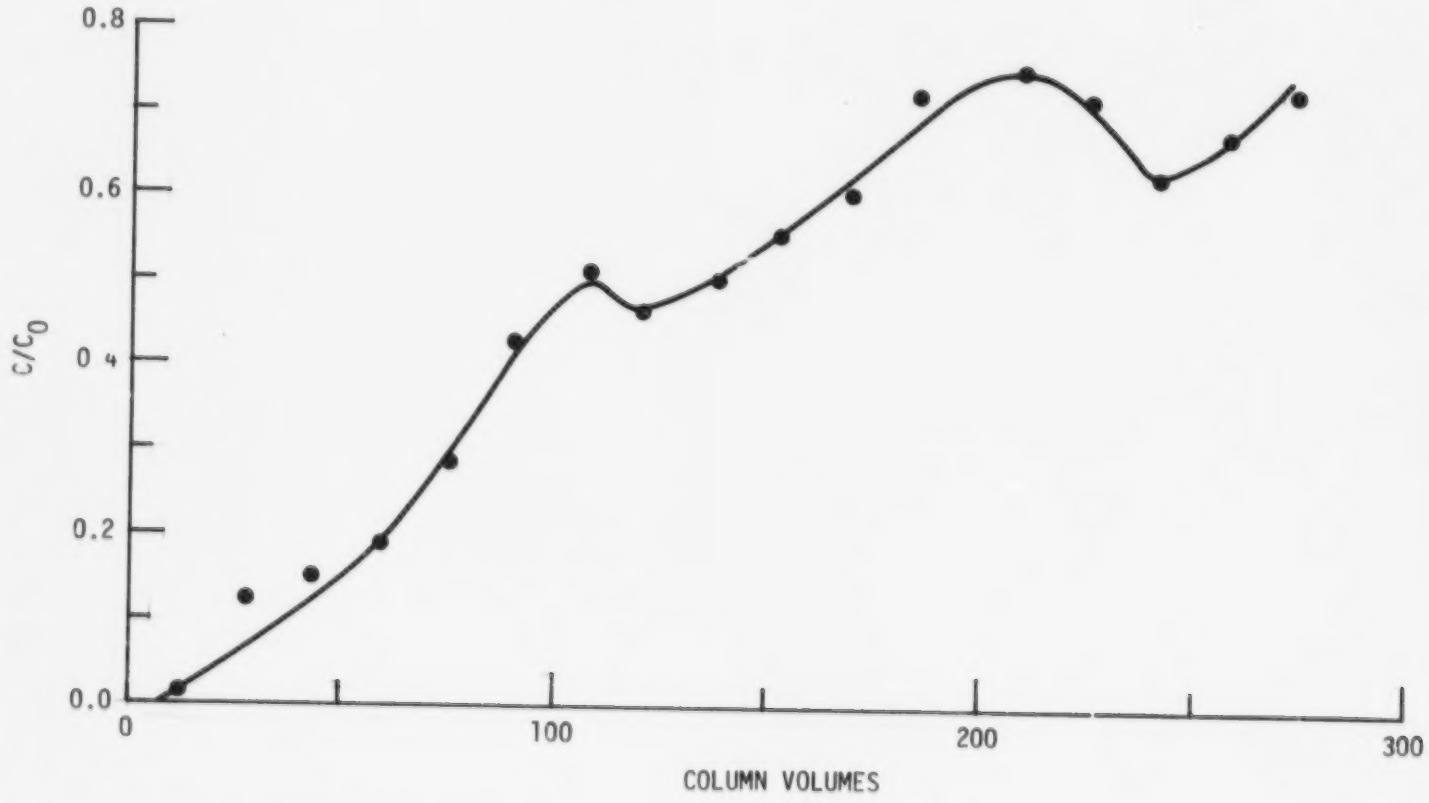


**Figure 7.** Ammonia breakthrough curve for column #1.

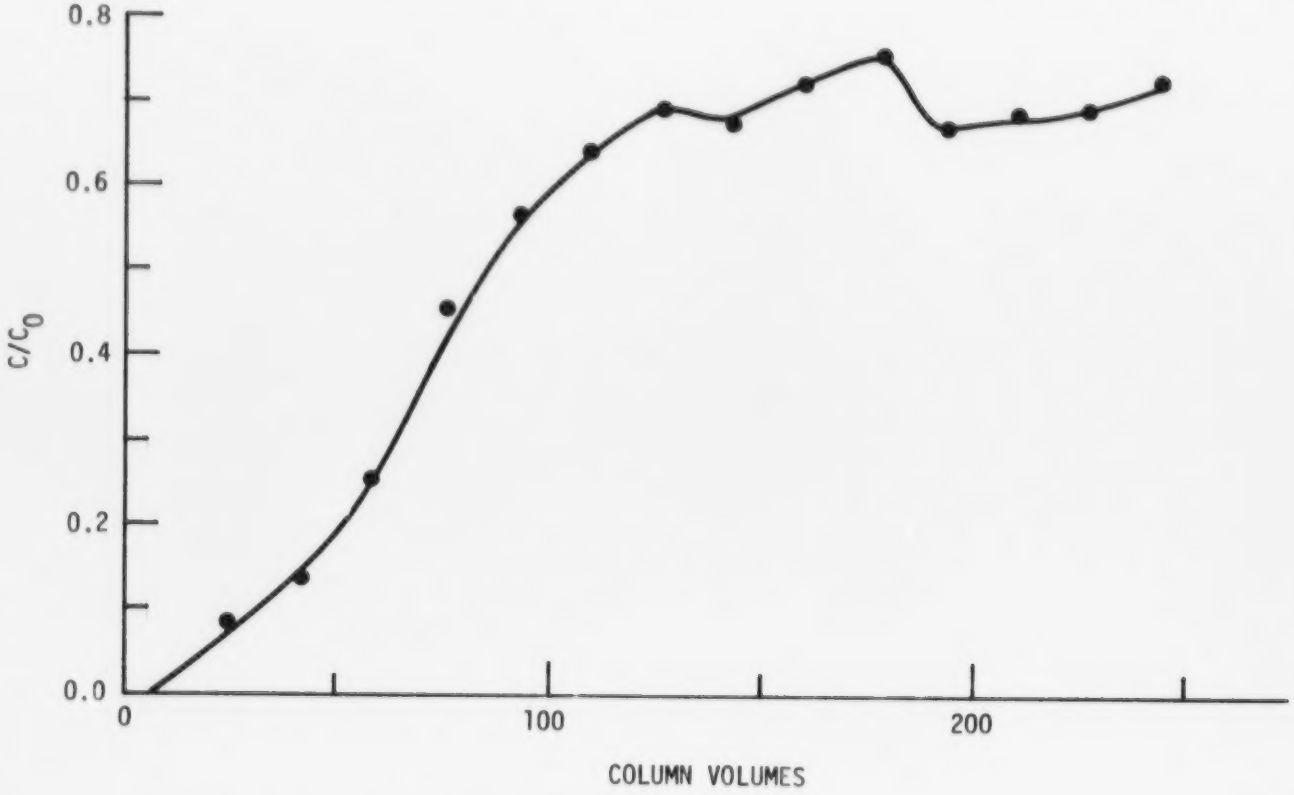


**Figure 8.** Ammonia breakthrough for column #2.

FIG 8

The smaller column was regenerated and reloaded for a total of 25 cycles at a flow rate of 5 ml/min. These were done with a continuous feed so as to avoid the above problem. Not all cycles were fractionated. Figure 9 presents the breakthrough curves for cycles 2, 6, 10, 15, 20 and 25, from the data in Appendix A. They indicated that only a small decrease in capacity occurred over the twenty-five cycles. This could be due in part to loss of exchanger or copper from the HZO. Analyses of selected fractions by atomic absorption spectrophotometry indicated no measurable amounts of copper were removed from the column.

It was found from these runs that after supposed breakthrough, a plateau was reached at $C/Co \sim 0.7$, which indicated that not all of the exchanger capacity had been used. Final effluents had an ammonia concentration of about 11 mg/l $NH_3$-N, even though the feed solution still contained 16.5 mg/l.

To learn more about this phenomenon, some of the data in Appendix A were used to determine the millimoles of ammonia removed in relation to the original millimoles of copper on the column. Table 9 contains the data from the experimental endpoint determined by visual examination of the figures. Table 10 contains similar data, only at constant column volumes for each cycle. These tables do indicate that the exchanger was removing near or more than the theoretical amount of ammonia based on the batch experiments. These values were near the results obtained from the column loading experiment at pH 11.5.

Returning to Tables 9 and 10, there was an apparent loss of capacity from the second through the twentieth cycle, with a small increase during the twenty-fifth cycle. Factors contributing to this type of behavior include: loss of exchanger, incomplete regeneration, loss of capacity, and variability between runs. Experimentally, there was no evidence to indicate that one of these reasons predominated.

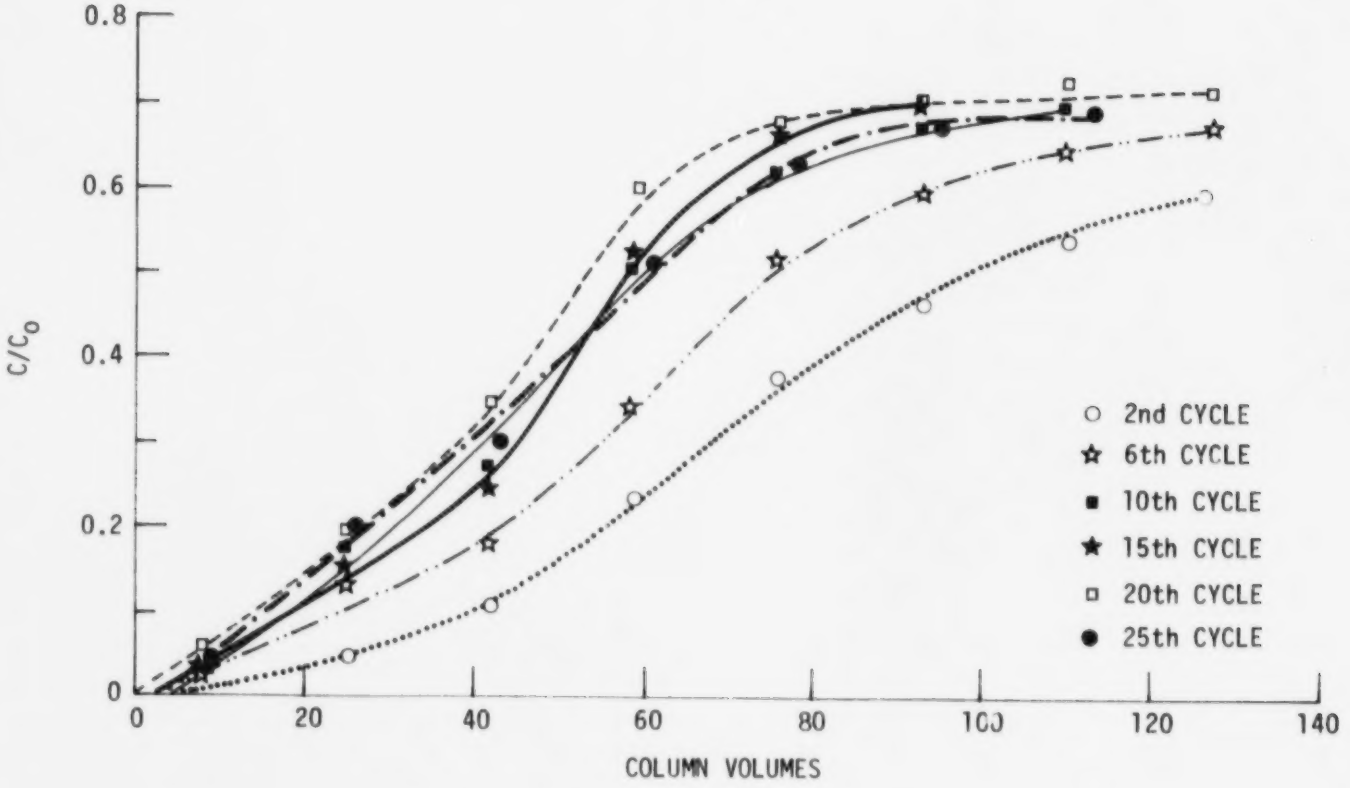


Figure 9. Ammonia breakthrough during repeated loading.

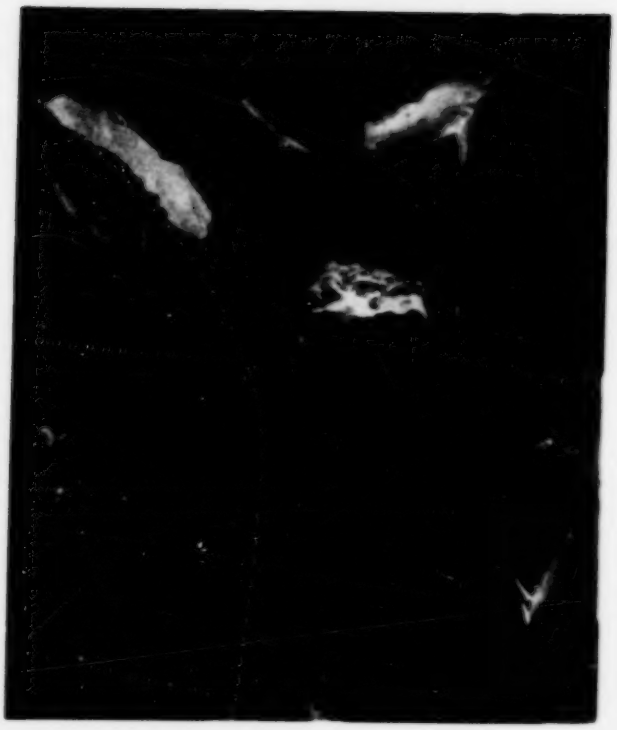

Figure 10. Scanning electron micrograph of hydrous zirconium oxide (100x).

Figure 11. Scanning electron micrograph of copper-hydrous zirconium oxide (100x).

Figure 12. Scanning electron micrograph of copper-hydrous zirconium oxide after 25 cycles (100x).

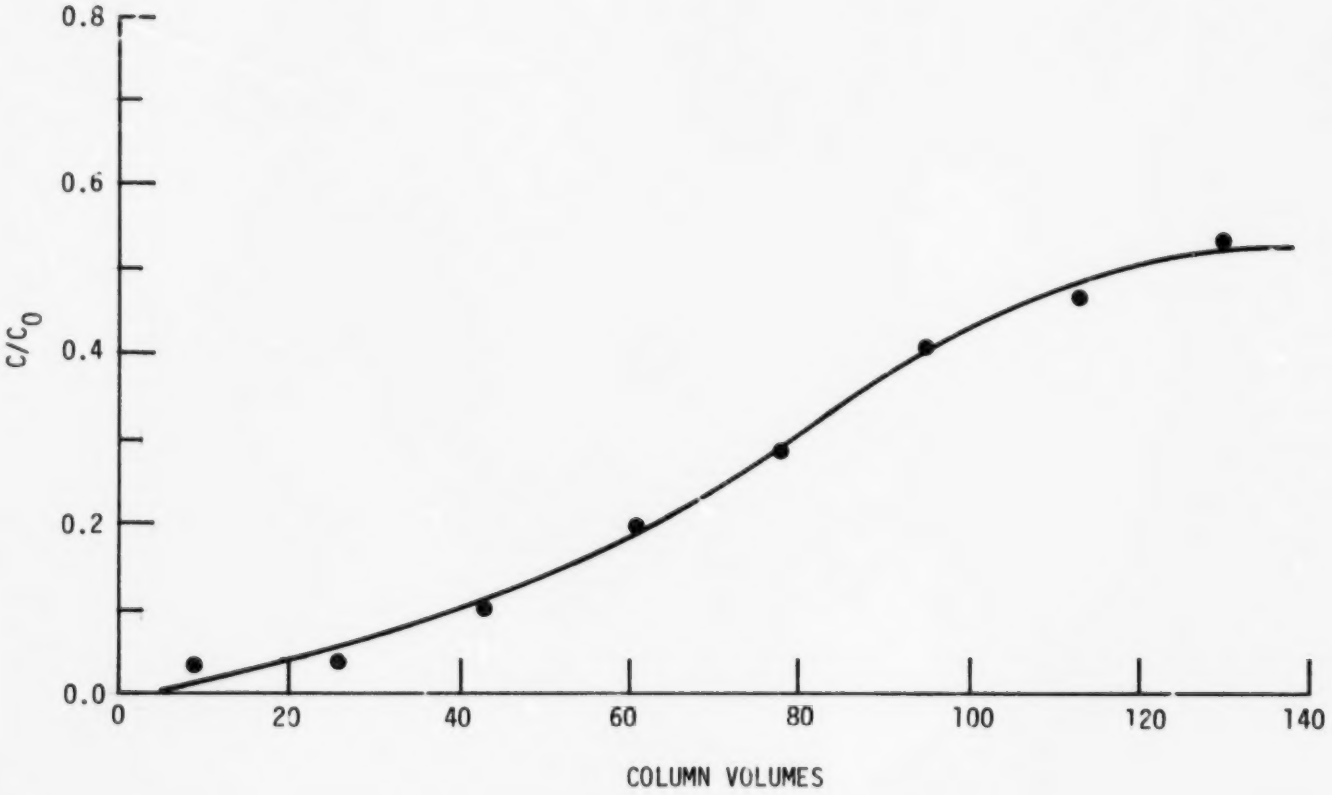


Figure 13. Ammonia breakthrough in presence of fluoride.

FIG. 13

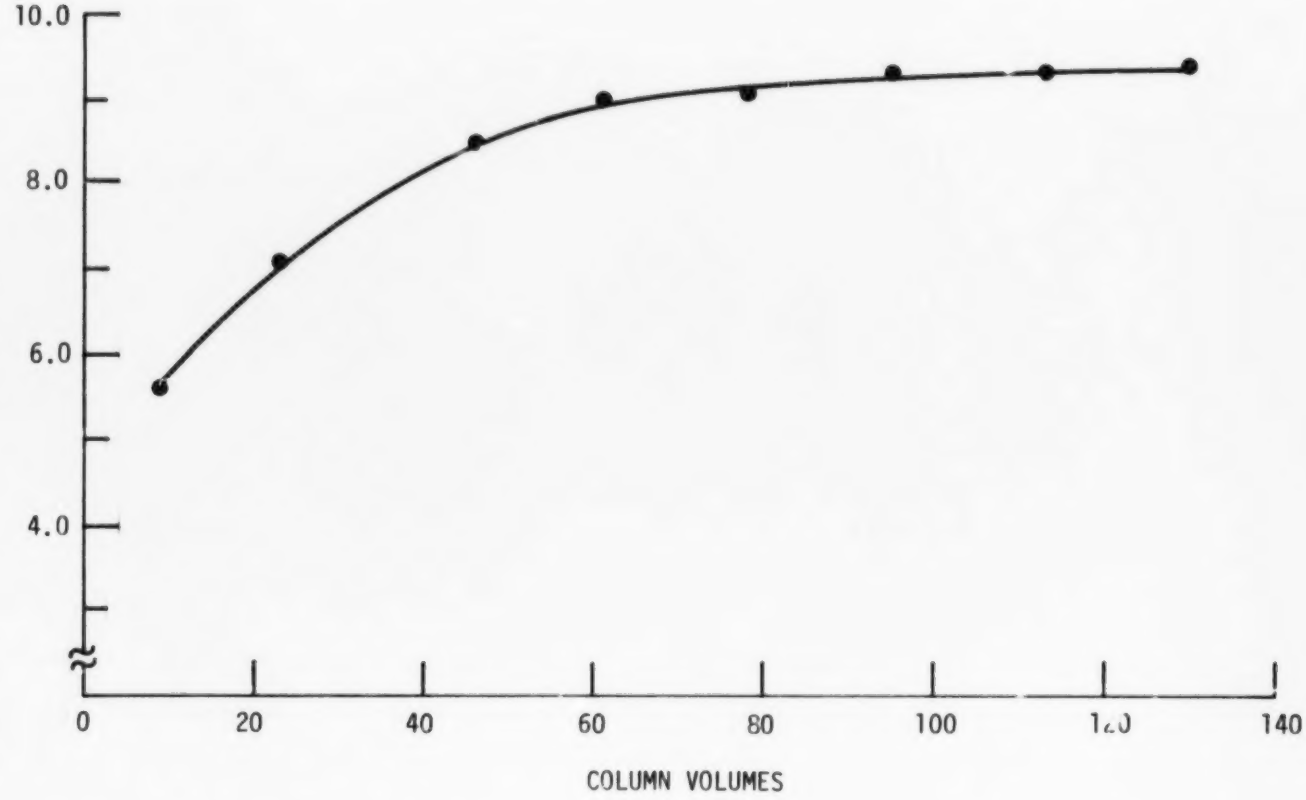


Figure 14. Fluoride uptake.

Table 9. AMMONIA REMOVED AT BREAKTHROUGH DURING REPEATED LOADING

| Cycle | Endpoint, column volumes | Wt. $NH_3$-N, mg | mg $NH_3$-N / gm exchanger | mmole $NH_3$ / mmole Cu |
|---|---|---|---|---|
| 2 | 143 | 24.9 | 1.00 | 0.102 |
| 6 | 127 | 20.2 | 0.81 | 0.083 |
| 10 | 110 | 16.0 | 0.63 | 0.066 |
| 15 | 93 | 15.0 | 0.60 | 0.062 |
| 20 | 110 | 15.2 | 0.61 | 0.062 |
| 25 | 113 | 16.2 | 0.65 | 0.067 |

Besides chemical stability, physical stability of the exchanger particles was also examined. Samples of the original HZO, the copper loaded HZO and the copper loaded HZO after 25 cycles were examined with the scanning electron microscope. The pictures are shown in Figures 10 through 12.

Copper loading had no apparent effect on the HZO particles. Comparing these to the particles after 25 cycles of ammonia loading and steam regeneration indicated that at worst, only minor deterioration occurred. In fact, there was no indication of any sort of particle break-up during operation. No change in pump pressure was needed, indicating very little change in pore size. Also, during back washing operations the solution stayed clear and no apparent fine fraction (smaller than 20-50 mesh) separated, though some of the small particles present did float to the top during backwashing and had to be rewetted before the column was packed.

Inorganic Constituent Effects

There are many impurities present in secondary wastewater that could affect the operation of a ligand exchange process designed for removing ammonia. One class of such species is the inorganic ions. Both primary

Table 10. AMMONIA REMOVAL DURING REPEATED LOADING

| Column volumes | Cycle | Wt. $NH_3$-N, mg | mmole $NH_3$/mmole Cu |
|---|---|---|---|
| 59 | 2 | 14.90 | 0.061 |
| 59 | 6 | 13.71 | 0.056 |
| 59 | 10 | 12.37 | 0.051 |
| 59 | 15 | 12.57 | 0.052 |
| 59 | 20 | 11.52 | 0.047 |
| 61 | 2[illegible] | 12.08 | 0.050 |
| 76 | 2 | 17.48 | 0.072 |
| 76 | 6 | 15.71 | 0.065 |
| 76 | 10 | 13.73 | 0.056 |
| 76 | 15 | 13.96 | 0.057 |
| 76 | 20 | 12.83 | 0.053 |
| 78 | 25 | 13.61 | 0.056 |
| 93 | 2 | 19.70 | 0.081 |
| 93 | 6 | 17.39 | 0.071 |
| 93 | 10 | 14.88 | 0.061 |
| 93 | 15 | 14.99 | 0.062 |
| 93 | 20 | 14.04 | 0.058 |
| 95 | 25 | 14.95 | 0.061 |

and secondary treatment are not intended to remove dissolved salts, though some of it may be adsorbed in the sedimentation process. Also, certain inorganic salts are added in primary treatment to aid in

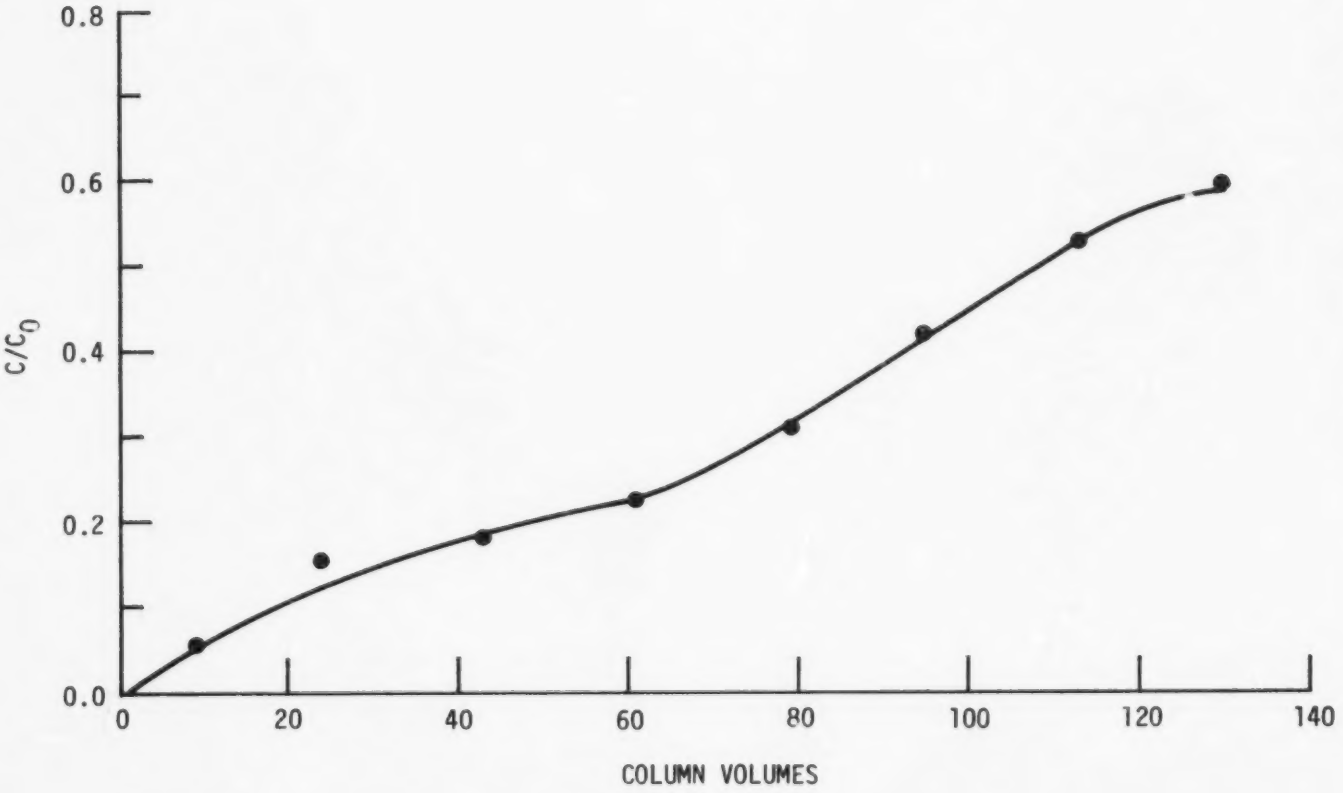


Figure 15. Ammonia breakthrough after fluoride treatment.

FIG 20

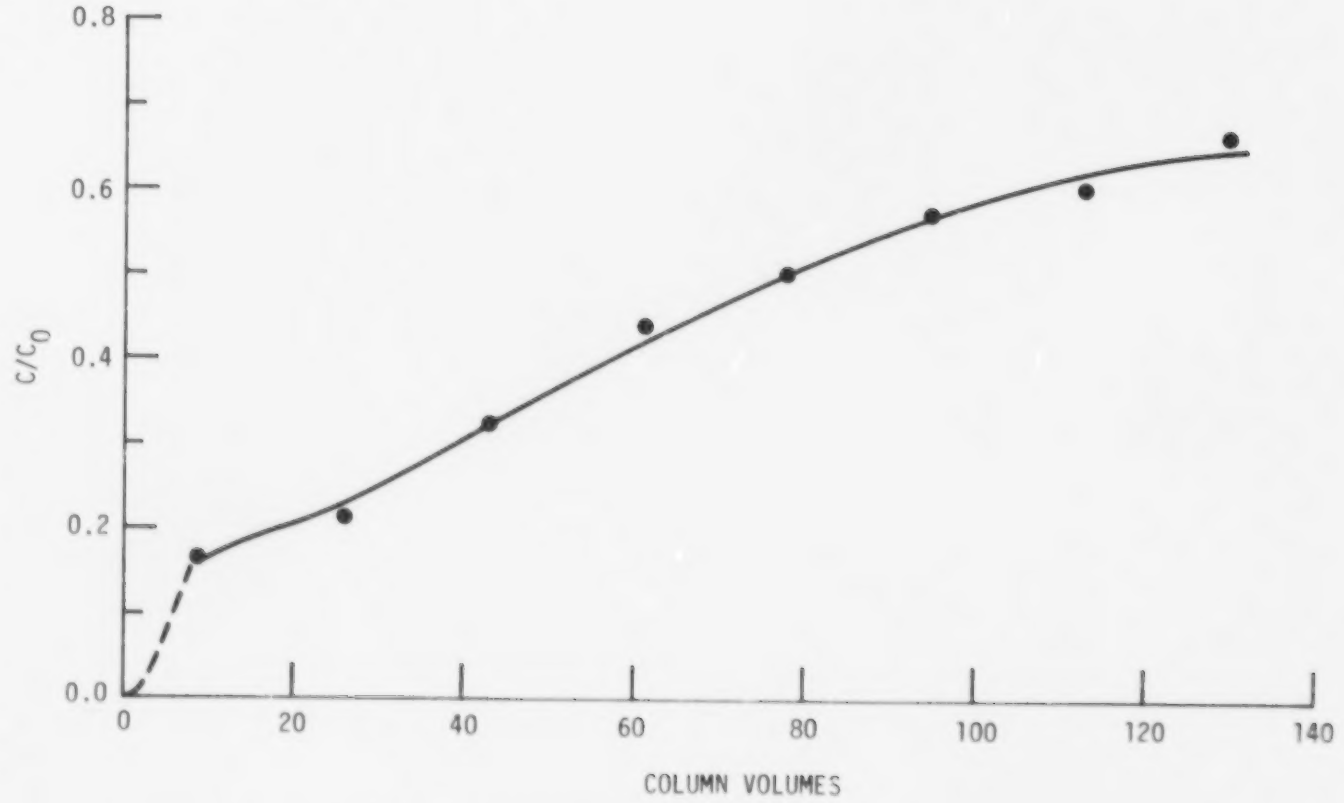


Figure 16. Ammonia breakthrough after ethylenediamine pretreatment.

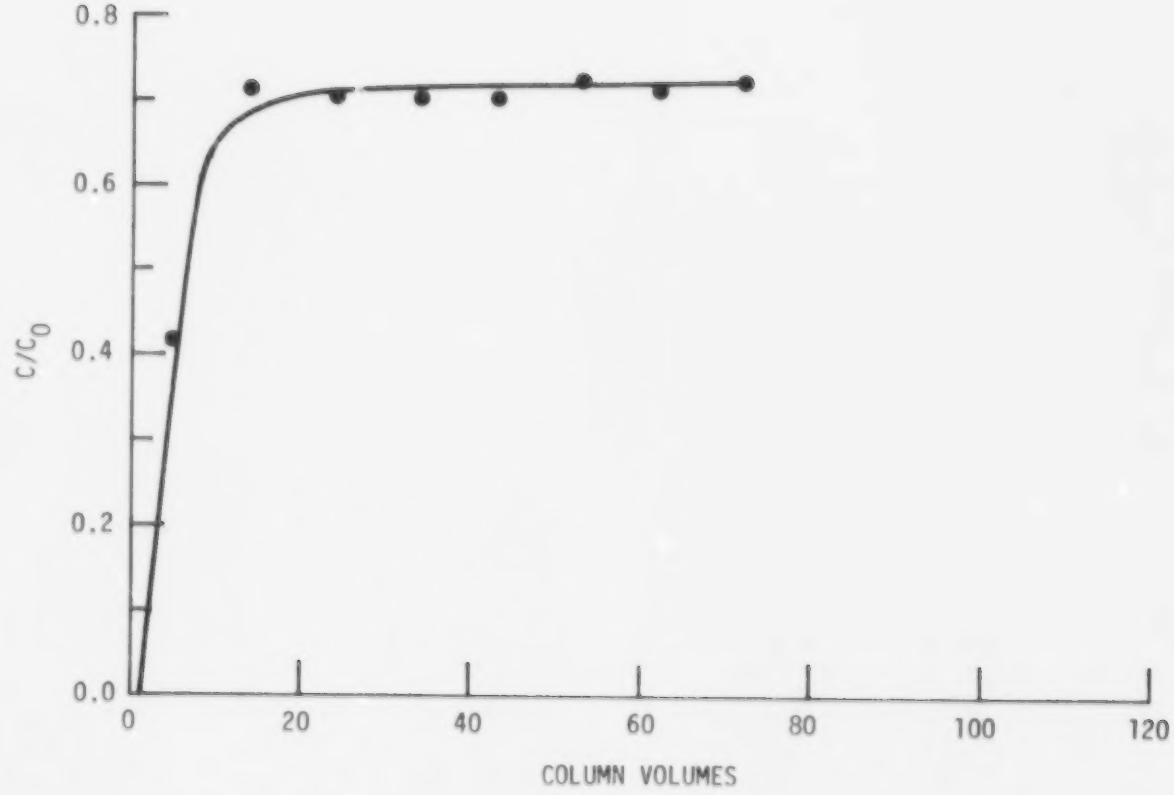


Figure 17. Ammonia breakthrough using wastewater - 1st cycle.

Fig 22

coagulation. The major inorganic constituents of secondary effluent and their approximate concentrations are:

| Ion | Concentration (mg/l) |
|---|---|
| Sodium | 135 |
| Potassium | 15 |
| Calcium | 60 |
| Magnesium | 25 |
| Chloride | 130 |
| Bicarbonate | 300 |
| Sulfate | 100 |
| Silicate | 50 |

Considering the ligand exchange process, the cations present in the wastewater could possibly compete with the copper, displacing it from the hydrous zirconium oxide, causing metal bleed. Returning to the ammonia removal equations,

$$\overline{R_2(Cu(H_2O)^{2+})} + NH_3 \longrightarrow \overline{R_2(Cu(NH_3)^{2+})} + H_2O \qquad (21)$$

the cations present in the feed solution might displace either the aquated copper or the amine copper complex from the HZO to a different degree. The properties of metal ions are known to be altered by the presence of coordinated ligands, as for example, stepwise stability constants.[12]

Anions present in wastewater would be expected to exert an effect on the ligand exchange process only. At pH 10 the hydrous zirconium oxide is a cation exchanger, and would not be expected to retain anions. Therefore, inorganic, anionic species, such as fluoride, cyanide, etc., that would compete with ammonia by forming stable copper complexes could be the most troublesome in a waste treatment operation.

The cations chosen for examination were sodium and calcium. Sodium ions are present at relatively high levels in secondary effluent. Also, the experiments on copper loading of HZO at high base concentrations indicated that sodium ions might be competitive. Calcium was also evaluated since it is divalent, as is copper, and is quite prevalent in wastewater. Also, if pH 10 were to be used, lime treatment of the wastewater would seem to be the obvious choice of alkalinity adjustment.

For the inorganic cations, batch equilibrations were performed. Separate experiments were performed on regenerated exchanger and loaded exchanger, which had been preequilibrated with a bath containing 16.5 mg/l $NH_3$-N at pH 10. Two grams of the exchanger were placed in a bath at pH 10 containing 100 mg/l of calcium or sodium ions. For $Na^+$, a non-coordinating buffer, tetramethyl ammonium hydroxide, was used to adjust the pH. After 24 hours, the supernatant solution was analyzed for copper and either calcium or sodium. In another set of experiments, 16.5 mg/l $NH_3$-N was added to the bath and after overnight equilibration, the ammonia content of the solution was determined. The data from Table 11 indicated that neither cation exhibited any effect on the ligand exchange process at the concentration examined. No copper was found in the solution. The calcium or sodium concentrations were very close to their original values. Also, when compared to previous results, the ammonia uptake by the unloaded exchanger was not altered. Therefore, the selectivity ratio for cupric ion or cupric-ammine ion in relation to calcium or sodium ion was quite high.

For the inorganic anions, it was felt that a batch equilibration study would not be adequate. Published satability constants[12] for aqueous systems could be used as a first approximation to determine if they would compete with ammonia for copper binding sites. An equally important problem, permanent loss of capacity rather than regenerable loss, needed to be determined. The inorganic anion chosen for examination

was fluoride. For the reaction

$$Cu^{2+} + F^- \longrightarrow CuF^+ \qquad (22)$$

the stability constant for the first fluoride complex is expressed by:

$$K = \frac{[CuF^+]}{[Cu^{2+}][F^-]} = 10^{1.2}\ M\text{-}1 \qquad (23)$$

A solution containing 16.5 mg/l $NH_3$-N and 10 mg/l $F^-$ was run through a ½ inch column containing 25.0 gms of exchanger containing 0.69 mmole Cu/gm HZO and fractionated. The ammonia and fluoride breakthrough curves are shown in Figures 13 and 14. The ammonia breakthrough was quite similar to those in the repetitive cycling. After 113 column volumes, 22.6 mg $NH_3$-N had been retained, corresponding to 0.093 mmole $NH_3$/mmole Cu. The fluoride breakthrough indicated that only small amounts of fluoride were retained on the column. Part of the general shape of the curve can be explained by the experimental technique. The columns were set up such that there was a water head over the column. This allowed for running the columns unattended, overnight in a down-flow direction with pump speed control. Therefore the first point or two in the breakthrough curve would contain a dilution factor.

Table 11. EFFECT OF SODIUM AND CALCIUM IONS ON COPPER BINDING TO HZO

| Regenerated exchanger[a] | | | | Loaded exchanger[a] | | | |
|---|---|---|---|---|---|---|---|
| $[Ca^{2+}]$,[b] mg/l | $[Na^+]$,[b] mg/l | [Cu(II)], mg/l | $[NH_3\text{-}N]$,[c] mg/l | $[Ca^{2+}]$,[b] mg/l | $[Na^+]$,[b] mg/l | [Cu(II)], mg/l | $[NH_3\text{-}N]$, mg/l |
| 100.9 | 0 | < 1 | 9.2 | 103 | 0 | < 1 | 15.8 |
| 0 | 107 | < 1 | 9.5 | 0 | 96 | < 1 | 16.8 |

[a] 0.69 mmole Cu/g HZO.
[b] Initial concentration of 100 mg/l.
[c] Initial concentration of 16.5 mg/l $NH_3$-N.

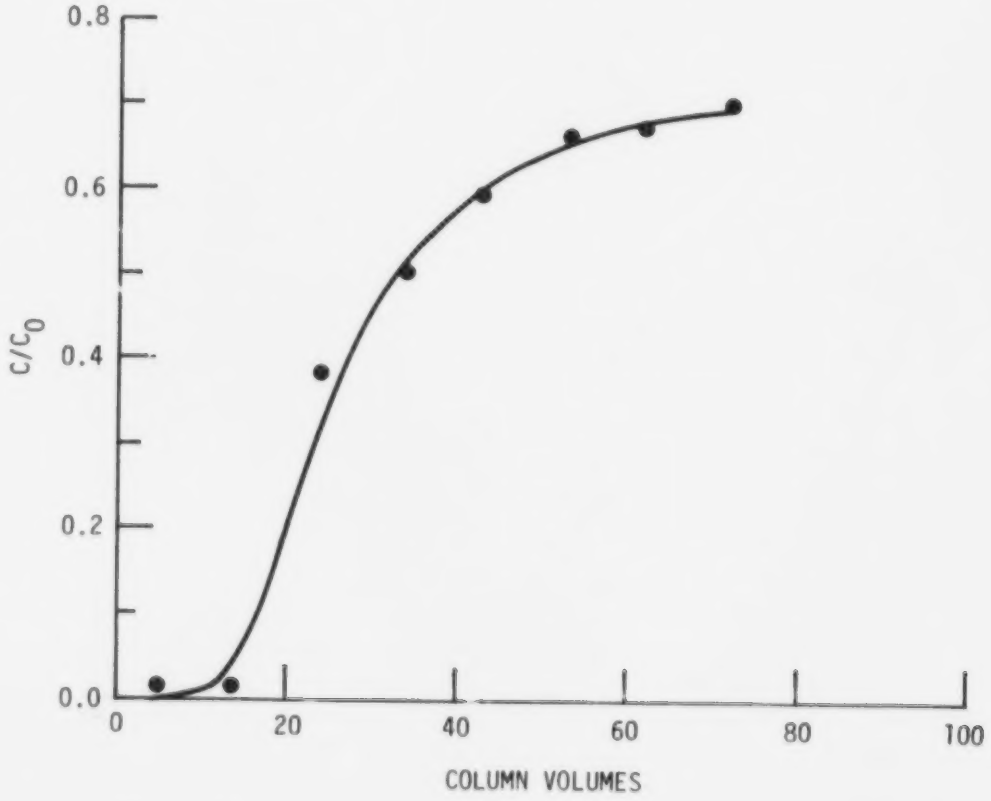


Figure 18. Ammonia breakthrough using wastewater - 2nd cycle.

FIG 23

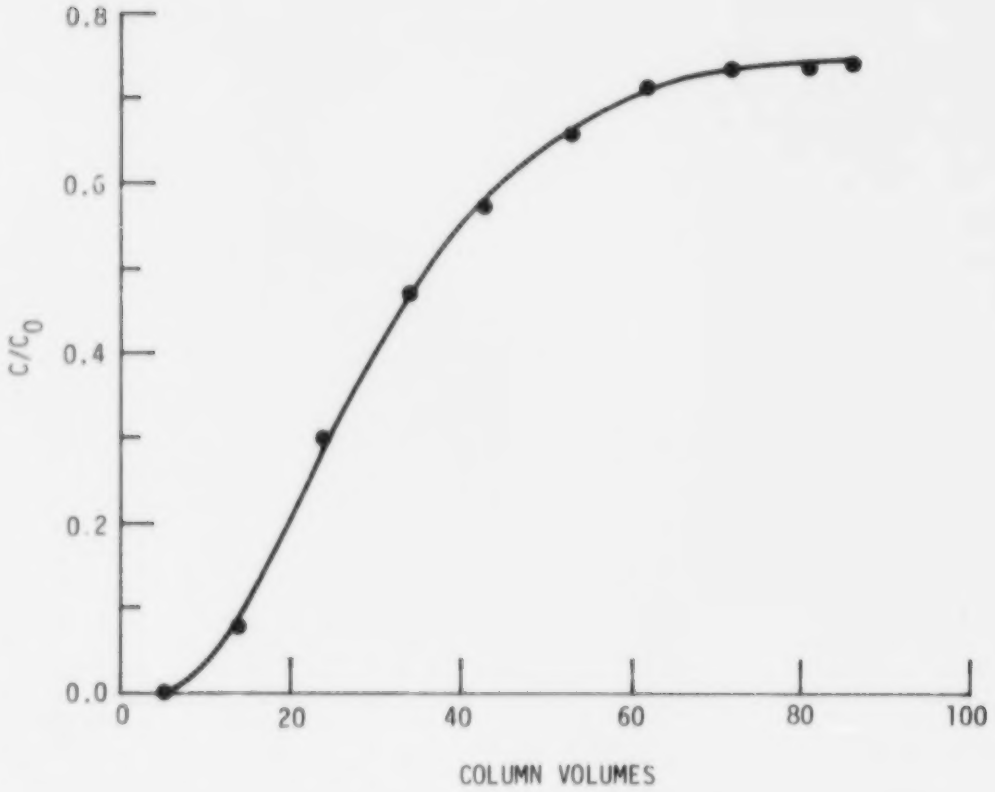


Figure 19. Ammonia breakthrough using wastewater - 3rd cycle.

The column was regenerated and a feed solution containing only 16.5 mg/l $NH_3$-N and no fluoride was used. This breakthrough curve is presented in Figure 15. Here, after 113 column volumes 21.1 mg $NH_3$-N were removed, or 0.087 mmole $NH_3$/mmole Cu. The fluoride had very little effect on the ability of the exchanger to remove ammonia during a subsequent cycle.

Sulfate and phosphate had been examined previously.[15] Addition levels of 100 mg/l and 10 mg/l respectively had no effect on ammonia capacity for two cycles of loading. Since chloride ion was used in adding the copper to the HZO, it can be presumed to have no effect either. Therefore, the common inorganic anions present in wastewater did not alter the ligand exchange process.

ORGANIC CONSTITUENTS EFFECTS

As with the inorganic anions, organic molecules present in wastewater would be expected to interfere mainly in the ligand replacement process. If the organic molecule was negatively charged, it could conceivably form a neutral or negatively charged copper complex. If this happened, then copper bleed could occur, since the HZO is a cation exchanger at the pH of operation. Organics with functional groups containing atoms such as S, O and N, where these heteroatoms have an unshared pair of electrons available, have the potential to form complexes with copper. These organics would not only affect the ammonia capacity during a loading cycle, but, if not regenerable, would cause permanent loss of capacity during the life of the exchanger.

Examination of the literature indicated very little knowledge on the composition of organics in secondary effluent.[25, 26] Those materials present were found to be at very low concentrations, usually at the micrograms/liter level. The organics that would tend to cause the most trouble in a wastewater operation would be those materials that form stable complexes with copper. Of these, other amines would appear to present the most problems. As a model compound, we chose to examine

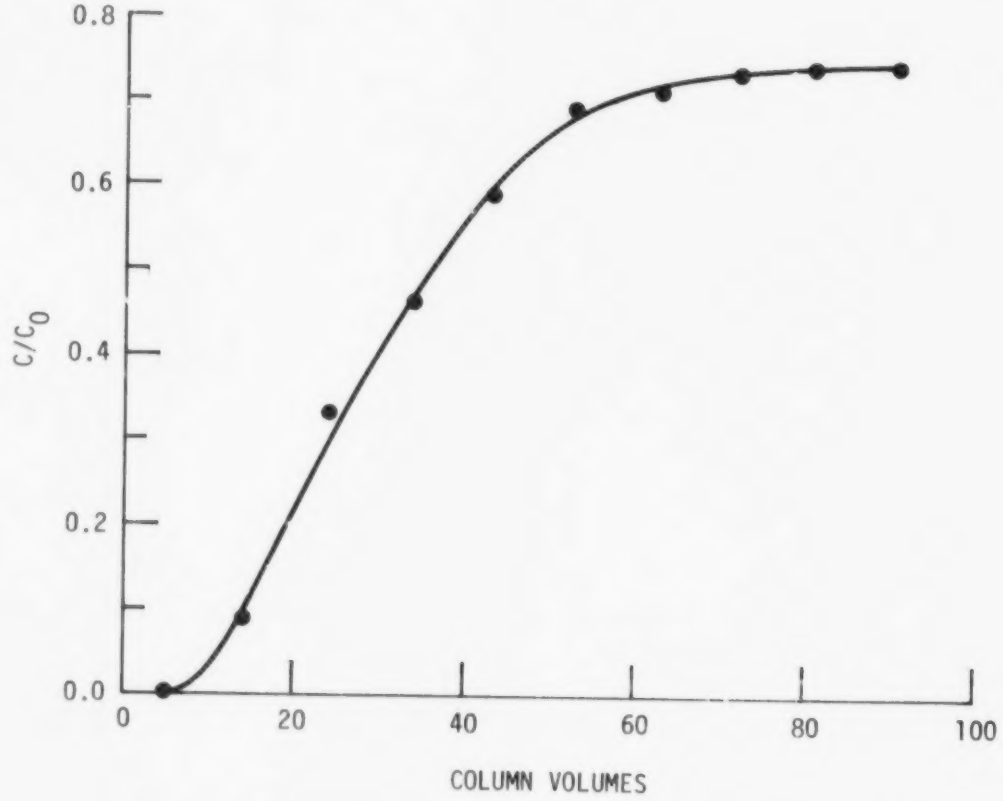


Figure 20. Ammonia breakthrough using wastewater - 4th cycle.

FIG 25

ethylenediamine ($NH_2CH_2CH_2NH_2$). There were two reasons for this choice. First, ethylenediamine (en) is of low molecular weight and exhibits a minimum of steric hinderance. Secondly, it would act as a bidentate ligand which would lend more stability to the copper complex due to the chelate effect.[27] This is exemplified by the stability constants for formation of the copper complex in aqueous solution:

$$Cu^{2+} + en \rightleftarrows Cu\ en^{2+} \tag{24}$$

$$K = \frac{[Cu\ en^{2+}]}{[Cu^{2+}]\ [en]} = 5.2 \times 10^{10}\ M^{-1} \tag{25}$$

while in comparison

$$Cu^{2+} + 2NH_3 \rightleftarrows Cu(NH_3)_2^{2+} \tag{26}$$

$$\beta_2 = \frac{[Cu(NH_3)_2^{2+}]}{[Cu^{2+}]\ [NH_3]^2} = 9.3 \times 10^{7}\ M^{-2} \tag{27}$$

Initially, a batch equilibrium experiment was performed to verify that ethylenediamine would be preferentially removed by the copper loaded HZO. To simplify the analytical procedures, en was determined by total organic carbon (TOC) analysis. An initial bath concentration of 50 mg/l en (22.0 mg/l TOC) and 16.5 mg/l $NH_3$-N at pH 10 was contacted with 2 grams of regenerated exchanger in one flask and with 2 grams of ammonia loaded exchanger in another. After 24 hour equilibration, a TOC determination was performed on the supernatant liquid. For the regenerated exchanger, an average value of 2.2 mg/l TOC was found. For the ammonia loaded exchanger this value was 7 mg/l TOC. Therefore, not only was most the en complexed by the copper, but in the case of the loaded exchanger, it was able to displace some of the ammonia.

To determine if ammonia exchange capacity was irreversibly lost, a fresh sample of exchanger (25 g; 0.69 mmole Cu/gHZO) was placed in a 1.27 cm

(½ inch) glass column and a 50 mg/l en solution at pH 10 was run through it at a rate of 5 ml/min until fully loaded. The column was then steam regenerated and the standard ammonium chloride solution (16.5 mg/l $NH_3$-N at pH 10) was then run through and fractionated. The breakthrough curve obtained is shown in Figure 16. A difference was noted between this breakthrough and one from the repetitive cycling experiments. The ammonia content in the initial fraction was higher than expected from a regenerated column. This would indicate that some column capacity had been lost. However, after 113 column volumes only 17.2 mg $NH_3$-N had been removed.

Ethylenediamine does have a deleterious effect on the ligand exchange process, though not as severe as would be expected from the stability constants. The ratio, $NH_3$ Cu, experimentally determined was low and corresponded to a column that had been repetitively loaded and regenerated for 15 or 20 cycles. However, the conditions that would be found in a municipal wastewater stream would not be as demanding. In secondary effluent, the concentrations of organics would be much lower than the 10 mg/l used. Also, these organics would not have the affinity for copper that ethylenediamine has, though some of them might not be steam regenerable.

USE OF MUNICIPAL WASTEWATER

In order to apply the findings from the previous experiments, actual secondary effluent was used on the column. The sample was obtained from the EPA pilot plant at the Blue Plains Wastewater Treatment Plant, Washington, D.C. It was the output from a lime clarifier and when obtained had a pH of 10. A 55-gallon sample was taken and stored in a polyethylene drum. The drum was allowed to stand for a day to remove the settleable solids. Then samples, as needed, were pumped from the top of the drum.

A column composed of 45 grams of exchanger containing 0.69 mmole Cu/g HZO was prepared. The wastewater was spiked with ammonium chloride before

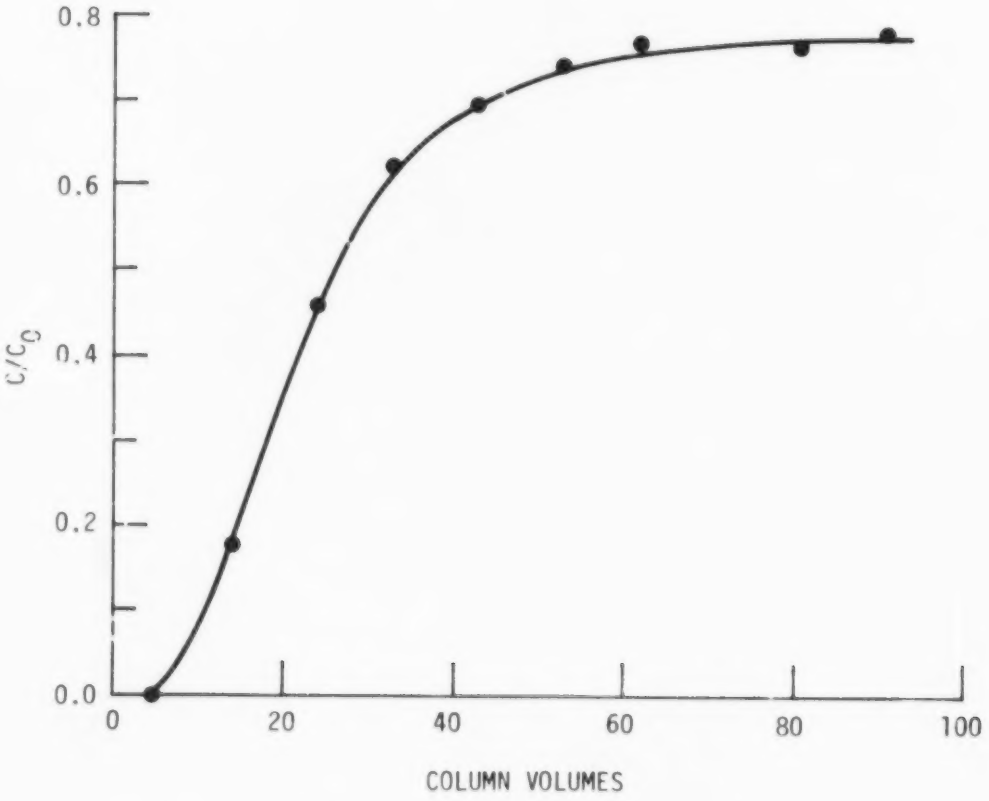


Figure 21. Ammonia breakthrough using wastewater - 5th cycle.

use in order to increase the ammonia content. From the average ammonia analysis of the feed, 23.8 mg/l $NH_3$-N, it was calculated that the original wastewater had an ammonia content of 7.3 mg/l $NH_3$-N. The column was run through five cycles of loading and regeneration, with each loading cycle at a feed rate of 5 ml/min being fracionated to construct a breakthrough curve as shown in Figures 17 through 21 from the data in Appendix B.

Operating difficulties were encountered in the first cycle, as evidenced by the rapid breakthrough of ammonia as seen in Figure 17. The second through fifth cycle appeared normal. No strange behavior was noted. Clogging of the column did not occur. There were no calcium carbonate deposits visible. Some of the data used to construct these curves are shown in Table 12. It was not until the fifth cycle that the data indicated some loss in capacity had occurred. This could be explained, at least in part, by loss of some of the exchanger, or loss of copper. The copper content of selected fractions were measured and found to be less than the sensitivity of the instrument, about 1 ppm. Non-regenerable loss due to build-up of organics attached to the copper could also explain the loss of capacity. This would become more evident with further cycles, if it occurred. Another interesting feature of these breakthrough curves was that they tended to plateau at a higher (C/Co) value. This would be expected, since the ammonia concentrations were higher than in the repetitive cycle experiments.

Another way of examining the data is to calculate the ratio, mmole $NH_3$/mmole Cu, as reported in Table 13. Comparing these results to those obtained in the repetitive loading experiment, Tables 9 and 10, and the ethylenediamine results, similarities were noted between the mmole $NH_3$/mmole Cu at apparent final breakthrough. The final capacity resembled the ethylenediamine results in that the value was lower than a column subjected only to a pure ammonium chloride solution. However, examining the efficiency, as determined by mmole $NH_3$/mmole Cu during column operation, it was seen that the column operated similarly with wastewater as it did with pure ammonium chloride (Table 10), even though

Table 12. AMMONIA REMOVAL FROM LIME CLARIFIED WASTEWATER

| Column volumes | Total $NH_3$-N removed, mg | | | |
|---|---|---|---|---|
| | Cycle | | | |
| | 2 | 3 | 4 | 5 |
| 10 | 5.8 | 5.9 | 5.9 | 5.9 |
| 19 | 11.7 | 11.4 | 11.3 | 10.8 |
| 29 | 15.3 | 15.6 | 15.3 | 14.1 |
| 38 | 18.3 | 18.7 | 18.5 | 16.3 |
| 48 | 20.7 | 21.2 | 20.9 | 18.1 |
| 57 | 22.7 | 23.3 | 22.6 | 19.6 |
| 67 | 24.6 | 25.2 | 24.4 | 21.0 |
| 77 | 26.4 | 27.0 | 26.0 | 22.6 |
| 86 | | 28.6 | 27.6 | 24.0 |
| 96 | | 30.1 | 29.1 | 25.3 |

the ammonia concentration was higher in the wastewater situation. This would indicate that the removal of ammonia was partially dependent on the feed rate, once a critical concentration of feed solution has been reached. And the increased capacity of the exchanger under different conditions resulted from a larger volume of feed solution passing through the column. Examination of the relationship between feed concentration and feed rate deserves further study.

Based on the previous results using solutions prepared from reagent grade chemicals, it was found that ammonia-spiked, lime treated secondary effluent behaved similarly. No problems were encountered due to calcium carbonate precipitation, either during the loading or the regeneration

cycle. Indications of any loss of capacity was not evident until the fifth and final cycle. Knowledge of the reasons for loss of capacity would aid in further optimization of ammonia removal, either by wastewater pretreatment or further operating changes.

Table 13. AMMONIA TO COPPER RATIO FOR THE WASTEWATER CYCLES

| Column volumes | $\frac{\text{mmole } NH_3}{\text{mmole Cu}}$ | | | |
|---|---|---|---|---|
| | Cycle | | | |
| | 2 | 3 | 4 | 5 |
| 10 | 0.013 | 0.014 | 0.014 | 0.014 |
| 19 | 0.027 | 0.026 | 0.026 | 0.024 |
| 29 | 0.035 | 0.032 | 0.035 | 0.032 |
| 38 | 0.042 | 0.043 | 0.042 | 0.037 |
| 48 | 0.047 | 0.048 | 0.048 | 0.041 |
| 57 | 0.052 | 0.053 | 0.052 | 0.045 |
| 67 | 0.056 | 0.058 | 0.056 | 0.048 |
| 77 | 0.060 | 0.062 | 0.059 | 0.052 |
| 86 | — | 0.065 | 0.063 | 0.055 |
| 96 | — | 0.069 | 0.066 | 0.058 |

## SECTION VI

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SECTION VII

## APPENDIX A - DATA FOR REPEATED LOADING EXPERIMENTS

Column 226-58, Aspect ratio=19.8; pH=10; Column volume=32 ml; Cycle 1

| Fraction | Total volume ml | Column volumes | Midpoint column volumes | $NH_3$-N, $x10^3$ gms | Total $NH_3$-N removed, $x10^3$ gms | $C/C_o$ |
|---|---|---|---|---|---|---|
| 2 | 500 | 16 | 12 | 0.07 | 8.17 | 0.017 |
| 4 | 1000 | 31 | 28 | 0.50 | 11.54 | 0.123 |
| 6 | 1500 | 47 | 43 | 0.62 | 22.62 | 0.150 |
| 8 | 2000 | 63 | 59 | 0.78 | 29.43 | 0.188 |
| 10 | 2500 | 79 | 75 | 1.23 | 35.50 | 0.298 |
| 12 | 3000 | 94 | 90 | 1.76 | 40.59 | 0.427 |
| 14 | 3625 | 114 | 108 | 3.16 | 45.74 | 0.511 |
| 15 | 4000 | 126 | 120 | 2.89 | 49.04 | 0.466 |
| 17 | 4500 | 142 | 138 | 2.08 | 53.12 | 0.504 |
| 19 | 5000 | 157 | 153 | 2.30 | 56.89 | 0.557 |
| 21 | 5500 | 173 | 169 | 2.50 | 60.46 | 0.606 |
| 23 | 6000 | 189 | 185 | 2.97 | 62.95 | 0.721 |
| 25 | 6500 | 204 | 200 | 3.10 | 65.13 | 0.752 |
| 27 | 7000 | 220 | 216 | 2.94 | 67.36 | 0.714 |

| Fraction | Total volume, ml | Column volumes | Midpoint column volumes | $NH_3$-N, $x10^{-3}$ gms | Total $NH_3$-N removed, $\pm 10^{3}$ gms | $C/C_o$ |
|---|---|---|---|---|---|---|
| 29 | 7500 | 236 | 232 | 2.58 | 70.24 | 0.625 |
| 31 | 8000 | 252 | 248 | 2.80 | 73.07 | 0.678 |
| 33 | 8500 | 267 | 263 | 3.00 | 75.54 | 0.727 |

Column 226-59, Aspect ratio=9.21; pH=10; Column volume=15 ml; Cycle 1

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 250 | 17 | 8 | 0.00 | 4.12 | 0.001 |
| 2 | 500 | 34 | 25 | 0.34 | 7.90 | 0.084 |
| 3 | 750 | 51 | 42 | 0.57 | 11.46 | 0.138 |
| 4 | 1000 | 67 | 59 | 1.06 | 14.53 | 0.256 |
| 5 | 1250 | 84 | 76 | 1.87 | 16.78 | 0.454 |
| 6 | 1500 | 101 | 93 | 2.33 | 18.57 | 0.566 |
| 7 | 1750 | 118 | 110 | 2.64 | 20.06 | 0.639 |
| 8 | 2000 | 135 | 127 | 2.84 | 21.34 | 0.689 |
| 9 | 2250 | 152 | 143 | 2.76 | 22.69 | 0.673 |
| 10 | 2500 | 169 | 160 | 2.96 | 23.85 | 0.718 |
| 11 | 2750 | 186 | 177 | 3.10 | 24.88 | 0.752 |
| 12 | 3000 | 202 | 194 | 2.55 | 26.46 | 0.617 |
| 13 | 3250 | 219 | 211 | 2.61 | 27.98 | 0.632 |
| 14 | 3500 | 236 | 228 | 2.63 | 29.47 | 0.638 |
| 15 | 3750 | 253 | 245 | 2.81 | 30.79 | 0.680 |

| Fraction | Total volume, ml | Column volumes | Midpoint column volumes | $NH_3$-N, $\times 10^3$ gms | Total $NH_3$-N removed, $\times 10^3$ gms | $C/C_o$ |
|---|---|---|---|---|---|---|
| 16 | 4000 | 270 | 261 | 2.52 | 32.40 | 0.610 |
| 17 | 4250 | 287 | 278 | 2.82 | 33.71 | 0.683 |

Column 226-59, Aspect ratio=9.21; pH=10; Column volume=15 ml; Cycle 2

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 250 | 17 | 8 | 0.02 | 4.10 | 0.007 |
| 2 | 500 | 34 | 25 | 0.18 | 8.04 | 0.044 |
| 3 | 750 | 51 | 42 | 0.43 | 11.74 | 0.104 |
| 4 | 1000 | 67 | 59 | 0.96 | 14.90 | 0.233 |
| 5 | 1250 | 84 | 76 | 1.54 | 17.48 | 0.374 |
| 6 | 1500 | 101 | 93 | 1.91 | 19.70 | 0.463 |
| 7 | 1750 | 118 | 110 | 2.22 | 21.61 | 0.538 |
| 8 | 2000 | 135 | 127 | 2.44 | 23.29 | 0.591 |

Column 226-59, Aspect ratio=9.21; pH=10; Column volume=15 ml; Cycle 6

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 250 | 17 | 8 | 0.13 | 4.00 | 0.030 |
| 2 | 500 | 34 | 25 | 0.53 | 7.59 | 0.129 |
| 3 | 750 | 51 | 42 | 0.72 | 11.00 | 0.175 |
| 4 | 1000 | 67 | 59 | 1.41 | 13.71 | 0.342 |
| 5 | 1250 | 84 | 76 | 2.13 | 15.71 | 0.516 |
| 6 | 1500 | 101 | 93 | 2.44 | 17.39 | 0.592 |

| Fraction | Total volume, ml | Column volumes | Midpoint column volumes | $NH_3$-N $x10^3$ gms | Total $NH_3$-N removed, $x10^3$ gms | $C/C_o$ |
|---|---|---|---|---|---|---|
| 7 | 1750 | 118 | 110 | 2.66 | 18.85 | 0.645 |
| 8 | 2000 | 135 | 127 | 2.79 | 20.19 | 0.676 |

Column 226-59, Aspect ratio=9.21; pH=10; Column volume=15 ml; Cycle 10

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 250 | 17 | 8 | 0.16 | 3.97 | 0.038 |
| 2 | 500 | 34 | 25 | 0.72 | 7.37 | 0.175 |
| 3 | 750 | 51 | 42 | 1.13 | 10.37 | 0.273 |
| 4 | 1000 | 67 | 59 | 2.13 | 12.57 | 0.516 |
| 5 | 1250 | 84 | 76 | 2.76 | 13.73 | 0.668 |
| 6 | 1500 | 101 | 93 | 2.98 | 14.88 | 0.721 |
| 7 | 1750 | 118 | 110 | 3.04 | 15.97 | 0.737 |
| 8 | 2000 | 135 | 127 | 3.04 | 17.06 | 0.737 |

Column 226-59, Aspect ratio=9.21; pH=10; Column volume=15 ml; Cycle 15

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 250 | 17 | 8 | 0.15 | 3.97 | 0.037 |
| 2 | 500 | 34 | 25 | 0.62 | 7.48 | 0.150 |
| 3 | 750 | 51 | 42 | 1.01 | 10.60 | 0.244 |
| 4 | 1000 | 67 | 59 | 2.16 | 12.57 | 0.522 |
| 5 | 1250 | 84 | 76 | 2.73 | 13.96 | 0.661 |
| 6 | 1500 | 101 | 93 | 3.10 | 14.99 | 0.752 |

Column 226-59, Aspect ratio=9.21; pH=10; Column volume=15 ml; Cycle 20

| Fraction | Total volume ml | Column volumes | Midpoint column volumes | $NH_3$-N $x10^3$ gms | Total $NH_3$-N removed, $x10^3$ gms | $C/C_o$ |
|---|---|---|---|---|---|---|
| 1 | 250 | 17 | 8 | 0.25 | 3.87 | 0.061 |
| 2 | 500 | 34 | 25 | 0.81 | 7.19 | 0.197 |
| 3 | 750 | 51 | 42 | 1.44 | 9.87 | 0.349 |
| 4 | 1000 | 67 | 59 | 2.47 | 11.52 | 0.600 |
| 5 | 1250 | 84 | 76 | 2.82 | 12.83 | 0.683 |
| 6 | 1500 | 101 | 93 | 2.91 | 14.04 | 0.706 |
| 7 | 1750 | 118 | 110 | 3.01 | 15.16 | 0.729 |
| 8 | 2000 | 135 | 127 | 2.94 | 16.34 | 0.714 |

Column 226-59, Aspect ratio=9.98; pH=10; Column volume=14 ml; Cycle 25

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 250 | 17 | 9 | 0.19 | 3.94 | 0.046 |
| 2 | 500 | 35 | 26 | 0.85 | 7.22 | 0.205 |
| 3 | 750 | 52 | 43 | 1.25 | 10.09 | 0.304 |
| 4 | 1000 | 69 | 61 | 2.13 | 12.08 | 0.516 |
| 5 | 1250 | 87 | 78 | 2.60 | 13.61 | 0.630 |
| 6 | 1500 | 104 | 95 | 2.79 | 14.95 | 0.676 |
| 7 | 1750 | 121 | 113 | 2.85 | 16.22 | 0.691 |

## APPENDIX B - DATA FOR WASTEWATER EXPERIMENTS

Column 226-78, Aspect ratio=16.2; pH=10; Column volume=26 ml; Cycle 1

| Fraction | Total volume, ml | Column volumes | Midpoint column volumes | $NH_3$-N, $x10^3$ gms | Total $NH_3$-N removed, $x10^3$ gms | $C/C_o$ |
|---|---|---|---|---|---|---|
| 1 | 250 | 10 | 5 | 2.47 | 3.46 | 0.417 |
| 2 | 500 | 19 | 14 | 4.29 | 5.11 | 0.723 |
| 3 | 750 | 29 | 24 | 4.20 | 6.85 | 0.707 |
| 4 | 1000 | 38 | 34 | 4.20 | 8.59 | 0.707 |
| 5 | 1250 | 48 | 43 | 4.20 | 10.33 | 0.707 |
| 6 | 1500 | 57 | 53 | 4.32 | 11.95 | 0.728 |
| 7 | 1750 | 67 | 62 | 4.26 | 13.62 | 0.717 |
| 8 | 2000 | 77 | 72 | 4.29 | 15.27 | 0.723 |

Column 226-78, Aspect ratio=16.22; pH=10; Column volume=26 ml; Cycle 2

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 250 | 10 | 5 | 0.09 | 5.84 | 0.016 |
| 2 | 500 | 19 | 14 | 0.09 | 11.68 | 0.016 |
| 3 | 750 | 29 | 24 | 2.29 | 15.34 | 0.385 |
| 4 | 1000 | 38 | 34 | 3.01 | 18.27 | 0.506 |

| Fraction | Total volume, ml | Column volume | Midpoint column volumes | $NH_3$-N, $x10^3$ gms | Total $NH_3$-N removed, $x10^3$ gms | $C/C_o$ |
|---|---|---|---|---|---|---|
| 5 | 1250 | 48 | 43 | 3.54 | 20.66 | 0.596 |
| 6 | 1500 | 57 | 53 | 3.95 | 22.66 | 0.665 |
| 7 | 1750 | 67 | 62 | 4.01 | 24.58 | 0.675 |
| 8 | 2000 | 77 | 72 | 4.17 | 26.36 | 0.702 |
| Column 226-78, Aspect ratio=16.22; pH=10; Column volume=26 ml; Cycle 3 | | | | | | |
| 1 | 250 | 10 | 5 | 0.00 | 5.93 | 0.001 |
| 2 | 500 | 19 | 14 | 0.47 | 11.40 | 0.079 |
| 3 | 750 | 29 | 24 | 1.79 | 15.55 | 0.301 |
| 4 | 1000 | 38 | 34 | 2.79 | 18.70 | 0.469 |
| 5 | 1250 | 48 | 43 | 3.41 | 21.23 | 0.575 |
| 6 | 1500 | 57 | 53 | 3.88 | 23.28 | 0.654 |
| 7 | 1750 | 67 | 62 | 4.01 | 25.21 | 0.675 |
| 8 | 2000 | 77 | 72 | 4.10 | 27.04 | 0.691 |
| 9 | 2250 | 86 | 81 | 4.35 | 28.63 | 0.733 |
| 10 | 2500 | 96 | 91 | 4.51 | 30.06 | 0.760 |
| Column 226-78, Aspect ratio=16.22; pH=10; Column volume=26 ml; Cycle 4 | | | | | | |
| 1 | 250 | 10 | 5 | 0.00 | 5.93 | 0.001 |
| 2 | 500 | 19 | 14 | 0.53 | 11.34 | 0.090 |
| 3 | 750 | 29 | 24 | 1.97 | 15.30 | 0.332 |
| 4 | 1000 | 38 | 34 | 2.76 | 18.48 | 0.464 |

| Fraction | Total volume, ml | Column volume | Midpoint column volumes | $NH_3$-N, $x10^3$ gms | Total $NH_3$-N removed, $x10^3$ gms | $C/C_o$ |
|---|---|---|---|---|---|---|
| 5 | 1250 | 48 | 43 | 3.51 | 20.9: | 0.591 |
| 6 | 1500 | 57 | 53 | 4.10 | 22.75 | 0.691 |
| 7 | 1750 | 57 | 62 | 4.23 | 24.46 | 0.712 |
| 8 | 2000 | 67 | 72 | 4.35 | 26.04 | 0.733 |
| 9 | 2250 | 86 | 81 | 4.39 | 27.59 | 0.739 |
| 10 | 2500 | 96 | 91 | 4.42 | 29.12 | 0.744 |

Column 226-78, Aspect ratio=16.22; pH=10; Column volume=26 ml; Cycle 5

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 250 | 10 | 5 | 0.00 | 5.93 | 0.001 |
| 2 | 500 | 19 | 14 | 1.03 | 10.84 | 0.174 |
| 3 | 750 | 29 | 24 | 2.73 | 14.05 | 0.459 |
| 4 | 1000 | 38 | 34 | 3.70 | 16.29 | 0.622 |
| 5 | 1250 | 48 | 43 | 4.13 | 18.10 | 0.696 |
| 6 | 1500 | 57 | 53 | 4.42 | 19.62 | 0.744 |
| 7 | 1750 | 67 | 62 | 4.57 | 20.98 | 0.770 |
| 8 | 2000 | 77 | 72 | 4.31 | 22.61 | 0.725 |
| 9 | 2250 | 86 | 81 | 4.51 | 24.04 | 0.760 |
| 10 | 2500 | 96 | 91 | 4.64 | 25.34 | 0.781 |